REMOVAL OF METHYL TERTIARY BUTYL ETHER (MTBE) FROM WATER USING MODIFIED AND NON-MODIFIED FLY ASH

BY

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To my family and friends

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ABSTRACT

Full Name : Segun Biodun Adebayo

Thesis Title : Removal of Methyl Tertiary Butyl Ether (MTBE) from Water Using Modified and Non-modified Fly Ash

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Methyl tertiary butyl ether (MTBE) is the most commonly used gasoline oxygenate and is been reported as a global groundwater contaminant. Several remediation techniques exist for its treatment, although with inherent limitations, making further studies promising. Fly ash (FA), a waste material derived from the combustion of coal or heavy liquid fuel, has been reported to show promising results in its application for adsorption of selected materials in aqueous solution. In this study, raw-FA, acid treated-FA and metal oxide (silver, iron and aluminum) impregnated-FA were assessed for their adsorption efficiencies for MTBE treatment in contaminated water. From experimental results, only silver oxide impregnated-FA showed adsorption of 24% removal of MTBE in aqueous solution, while the other tested adsorbent materials showed <10% removal. The pH of the solution was found to have insignificant effect on MTBE removal when non-modified fly ash was applied. However, the more acidic solution showed better adsorption with the Ag_2O impregnated fly ash. Also, Ag_2O-FA showed optimum adsorption at 2 hours of contact, and using 50 mg of adsorbent.

MASTER OF SCIENCE DEGREE
KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN, SAUDI ARABIA

ملخص الرسالة

الاسم الكامل: سيجون بيودن اديبايو

عنوان الرسالة: إزالة مركب الميثيل ثلاثي البيوتيل ايثر من الماء باستخدام الرماد المعدل وغير المعدل.

التخصص: العلوم البيئية

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يعتبر مركب الميثيل ثلاثي البيوتيل ايثر (MTBE) من المواد الشائعة الاستخدام كمادة مضافة الى الوقود لتحسين عملية الاحتراق. كما اثبتت العديد من التقرير انه احد ملوثات المياه الجوفيه. توجد العديد من التقنيات التي تساعد علي التخلص منه بالرغم من وجود العديد من التحديات التي تواجه هذه التقنيات. بالتالي فان مزيدا من الدرسات تعطي الامل للتخلص منه كملوث للماء. لقد اشارت دراسات سابقة بان الرماد الذي يعتبر من مخلفات الناتجه من حرق الفحم او الوقود قد يعطي نتائج مبشره في التطبيقات التي تساعد علي امتصاص الملوثات . في هذه الدراسه تم اختبار قدرة الرماد المعالج بالحامض والمغلف بالعناصر المؤكسده مثل الحديد والالمنيوم والفضة في التخلص من مركب (MTBE) في المياه الملوث. أثبتت نتائج الدراسة ان الرماد المغلف باوكسيد الفضة هو الذي اظهر نتيجة امتصاص حوالي 24% من ام. تي.بي. اي. من المياه, بينما لم تستطع الاشكال الاخرى من الرماد المغلفة باوكسيد الالمنيوم والحديد من امتصاص اكثر من 10% من المركب. كما دلت النتائج انه في حالة استخدام الرماد غير المعدل فانه حموضه المحلول ليس لها تاثير واضح في ازالة مركب(MTBE). وقد ثبت انة في حالة تطبيق الرماد المعدل في المحاليل الاكثر حموضه هنالك امتصاص جيد مع وجود الرماد المغلف باكسيد الفضة وافضل الامتصاص تم الحصول عليه بعد ساعتين وباستخدام 50 مليجرام من الرماد المغلف باكسيد الفضه.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ـ المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

1.1 Background

The production of reformulated gasoline emerged from the desire to improve air quality, by reducing smog problems and increasing oxygen content of gasoline. The environmental threats from the use of tetra-ethyl lead in reformulated gasoline prompted the introduction of methylene tertiary butyl-ether (MTBE) and ethanol as additives to gasoline (Iob *et al*., 1998). MTBE was found compatible with all types of automotive and tank liner materials and its addition resulted in reduced levels of carbon monoxide and hydrocarbons emitted (Kelley, 2004). These features prompted its wide use as an oxygenated additive and octane enhancer in gasoline. Saudi Basic Industries Corporation (SABIC), Saudi Arabia is the largest producer of MTBE in the world (SABIC, 2014). However, as in a classic case of the law of unintended consequences, MTBE which is being added to unleaded gasoline as octane enhancer, but is now considered to pose significant risks to groundwater and drinking water sources.

Saudi Arabia has an arid climate with an average annual rainfall of 100 mm, having groundwater as the major source of water supply for all purposes. Water is a scarce and extremely valuable resource and given the country's rapid population growth, the demand on the limited available water sources is increasing. Rainfall is very low, unpredictable as

well as highly irregular, but can be very intensive during local storms (Abdullah and Al-Mazroui, 1998). Generally, the rate of precipitation is lower than that of evapotranspiration, with evapotranspiration driven principally by high temperature and dry wind. The aridity of this region is a result of climatic influences which include the general circulation of the air, distance from a moisture source and local factors such as mountain barriers. Since the water resource is a major factor for domestic, industrial and agricultural activities, the rational development of this resource should be considered as one of the highest priorities in areas with arid conditions like Saudi Arabia (Mahmoud and Sen, 1993). Given the peculiar water demand situation of Saudi Arabia, the need to protect the limited available water sources cannot be overemphasized. As a result of the high volume production of MTBE and its broad utilization in the Kingdom, accidental discharge from the production through to consumption point becomes inevitable. This serves as a key motivation for researches into removal of MTBE from the water sources in Saudi Arabia.

In addition to removal efficiency, cost is a major consideration for choice of any remediation technology and the use of modified fly ash for MTBE removal has the potential to fulfil these key requirements. Fly ash is a readily available waste material from the combustion of coal or heavy liquid fuel during the generation of electricity. Very few countries utilize a major proportion of the fly ash waste generated from this process. The most widely applied use is in the cement industry, and the excess fly ash being disposed of in landfills. Fly ash closely resembles volcanic ashes used in production of the earliest known hydraulic cements about 2,300 years ago (Patil *et al.*, 2010). The fly ash used in this research was collected from heavy liquid fuel powered

electricity generating power plants operated by Saudi Aramco, where liquid fuel is burned and producing a mineral residue captured from the exhaust gases. The fly ash consists primarily of silica, alumina and iron. The source local industry produces millions of tonnes of fly ash per year, making it readily available.

1.2 Statement of the Problem

An important property of MTBE is its high solubility in water and poor sorption to soil. Hence, when compared to other gasoline components, MTBE dissolves quickly into groundwater and migrates farther and faster following accidental gasoline release, coupled with its poor natural biodegradation property. Remediation technologies such as adsorption with activated carbon or charcoal filters, air stripping, and bioremediation have recorded varying levels of success. Although each technique is characterized by its inherent limitations, which creates the opportunity for further research into the removal of MTBE from groundwater and other water sources.

1.3 Significance of the Study

Sustainable development in Saudi Arabia entails maintenance of the limited available water sources. Given that MTBE has been established as an environmental contaminant of concern globally, there is a need to explore possible techniques to assuage the risk to groundwater sources (Cater et al., 2000). The groundwater sources in Saudi Arabia are the major sources of drinking water; therefore, even a low level of MTBE can make water from such sources undrinkable given its offensive taste and odour. Leakage from above and below ground storage and conveyance facilities, spillage and evaporation

during manufacturing and transportation of MTBE containing gasoline are the major routes of entry for MTBE into the environment. At concentrations as low as 2.5 µg/L, MTBE has been reported to exhibit turpentine-like odour (Cater *et al*., 2000). High water solubility (50,000 mg/L), low soil and aquifer adsorption, poor natural biodegradation compared to other fuel hydrocarbons, high mobility and persistence as it travels through the groundwater system have equally made MTBE a contaminant of concern. MTBE has been classified as a potential human carcinogen by the US Environmental Protection Agency (EPA) and suggestion has been made that MTBE concentration between 20 and 40 µg/L in drinking water could cause adverse health effects (USEPA, 1997b).

This study focused on the use of non-modified and modified forms of fly ash which is a waste product from a local industrial power plant for the removal of MTBE in contaminated water sources. The utilization of a local industrial waste serves as a form of waste reuse, therefore enhancing the waste management process in the Kingdom. Also, the study outcome served as a cost effective alternative to the use of activated carbon in the removal of MTBE from contaminated water sources and increased scientific knowledge on removal of MTBE in water sources.

1.4 Research Objectives

The main objective of this research was to assess the efficiency of modified and non-modified fly ash for the removal of MTBE from contaminated water.

The specific objectives were:

1. To demonstrate removal of MTBE from contaminated water using modified and non-modified fly ash under bench-scale conditions.
2. To study the effect of solution conditions such as pH, fly ash dosage, contact time, MTBE concentration, and mixing rates on the adsorption efficiency.
3. To evaluate the adsorption kinetics under the optimum treatment conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 Methyl Tertiary Butyl Ether (MTBE)

Oxygenated compounds (oxygenates) are oxygen-rich additives to gasoline meant to increase the oxygen content and enhance combustion, thereby decreasing vehicular carbon monoxide (CO) emissions. The Clean Air Act (CAA) Amendments of 1990 in the United States mandate seasonal or year-round use of oxygenates in specific parts of the country. This Act has been adopted by several countries in the bit to improve air quality and minimize CO emission. MTBE is the most widely used oxygenate, followed by ethanol (Rick *et al*., 2001). Gasoline to which MTBE is added is usually referred to as oxygenated gasoline and MTBE has been added as octane enhancer since the late 1970's. Its production and use have recorded significant increase thereafter. Low cost and readily simple production makes MTBE preferable to other oxygenates like ethanol (Jacobs *et al*., 2000; Rick *et al.,* 2001).

2.2 Production of MTBE

In the composition of MTBE, one carbon atom is that of a methyl group ($-CH_3$) and the other is the central atom in a tertiary butyl group ($-C(CH_3)_3$). The reaction of methanol made from natural gas with isobutylene (2-methyl-1-1propene) in liquid state, using an

acidic catalyst at 100°C leads to the production of MTBE. Isobutylene is made from butanes derived from petroleum (USEPA, 1994).

Chemical equation for MTBE formation from isobutylene:

$$CH_3OH + CH_2 = C(CH_3)CH_3 \Rightarrow CH_3OC(CH_3)_2CH_3$$

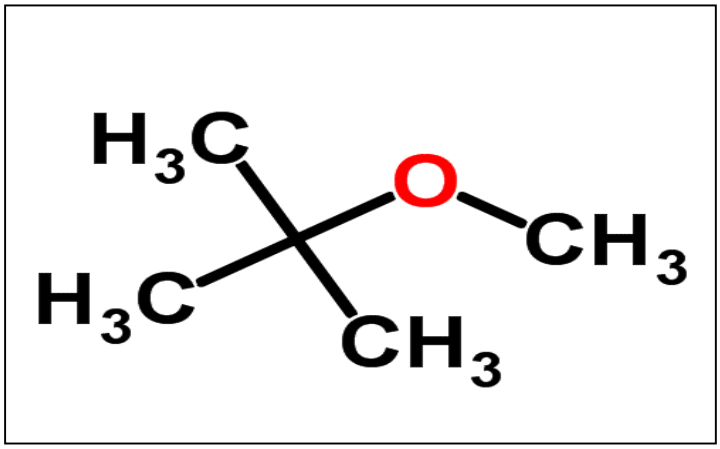


Figure 2.1: Two Dimension Chemical Structure of MTBE
(Source: http//www.chemspider.com)

2.3 Uses of MTBE

The largest use for MTBE is as a gasoline additive, accounting for almost all its consumption in Saudi Arabia and in the United States. Also, in the production of high purity isobutylene, small amounts of MTBE are used as chemical intermediate (USEPA, 1994). Limited amounts are also used medically to dissolve gallstones and as a laboratory solvent for designated EPA analytical methods (ATSDR, 1996).

2.4 Properties of MTBE

Not naturally occurring, but derived from methanol, isobutylene or other petroleum refinery products, MTBE is an oxygenated volatile organic compound. MTBE is a colorless, flammable liquid with a strong unpalatable odor, similar to turpentine

(ATSDR, 1996; Squillace *et al.,* 1995). Table 2.1 summarizes some of the important physical and chemical properties of MTBE.

Table 2.1. Summary of Physical and Chemical Properties of MTBE

PROPERTY	VALUE
CAS Registry Number	1634-04-4
Molecular Formula	$C_5H_{12}O$
Synonyms	Tertiary-butyl methyl ether, t-butyl methyl ether, methyl t-butyl ether, 2-methyoxy 2 methyl propane, 2-methyl-2 methoxypropane, methyl-1,1-dimethylethyl ether
Molecular Mass (g/mole)	88.15
Boiling Point (^oC)	55 to 56
Melting Point (^oC)	-109
Flashpoint Temperature (^oC)	-2
Auto Ignition Temperature (^oC)	373
Density (g/mL)	0.740
Water Solubility (mg/L) @ 25^oC	22,200 to 54,000
Henry's Law Constant @ 25^oC	0.026 ($cm^3w/cm^{-3}g$)
Vapor Pressure	27.6kPa (4.05 psi) @ 20^oC

(Source: Jacobs *et al.,* 2000)

2.4.1 Solubility in Water

Water solubility is considered probably the most important chemical property affecting the partitioning of organic compounds between water and subsurface solids. MTBE is less dense than water and highly soluble in water. Its solubility usually ranges between 23,200 to 54,000 mg/L, with pure MTBE having solubility of approximately 50,000 mg/L. MTBE is very water soluble compared to other components of gasoline, with the next most soluble component of gasoline being benzene, which has a solubility of 1,780 mg/L (Mackay *et al.,* 1993).

2.4.2 Volatility

The tendency of a constituent to partition between aqueous and vapor phases is described by a measure of its Henry's law constant as well as other environmental factors. MTBE has low Henry's law constant of 0.022 at 25^{o}C, hence it has greater affinity to stay in the aqueous phase and pose difficulties to removal by aeration. When compared to other gasoline components such as benzene, MTBE is 10 times less volatile than benzene which has Henry's constant of 0.22 at 25^{o}C (Howard *et al.,* 1990).

2.4.3 Adsorption

This is a measure of partitioning tendency of a dissolved constituent between sorbed and aqueous phases. It depends on the chemical organic-carbon partition coefficient (K_{OC}) and the fraction of organic carbon in the soil (f_{OC}). The high solubility of MTBE in water is major limitation to its sorption capacity. MTBE has tendency for sorption to solids with high organic carbon contents as compared to those with little or no organic carbon content (Jacobs *et al.,* 2000). When compared to other gasoline components, MTBE tends

to travel much faster due to its lesser organic-carbon partition coefficient K_{OC} (11 mg/L), approximately 7 times less than the 80 mg/L of benzene (Squillance *et al.,* 1996).

2.4.4 Odor and Taste

At low concentrations of 5 to 20 µg/L, a distinctive unpleasant taste and turpentine odor of MTBE can be sensed by humans. Consequently, the U.S. Environmental Protection Agency's advisory level for MTBE ranges from 20 to 40 µg/L (USEPA, 1997b).

2.4.5 Human Exposure to MTBE

Breathing in air in the process of pumping gasoline containing MTBE or pouring gasoline into engines such as lawn mowers is a route of exposure. Similarly, breathing of exhaust fumes while in a vehicle or near a road is another exposure route for humans. Another important pathway is drinking, swimming, or showering in water contaminated with MTBE. Given that MTBE use in gasoline is being phased out in the U.S, drinking water contamination is the most likely source of exposure for most people (ACS, 2011). The other routes are still very applicable in Saudi Arabia and other countries where MTBE is still being used as the choice oxygenate.

2.4.6 Environmental Release, Transport and Fate of MTBE

Accidental release of MTBE may occur at industrial sites during manufacturing, mixing with gasoline, storage, distribution, spills, or emissions at automotive service stations. The Toxics Release Inventory for the U.S. in 1992 reported MTBE release as 2.8 million pounds, 100 thousand pounds, 68 thousand pounds and 288 pounds to air, surface water, underground injection sites and land, respectively (TRI92, 1994).

As a result of the high volatility of MTBE, it is expected to volatilize rapidly from soil and surface water. However, MTBE leaking from underground gasoline storage tanks may not readily reach the atmosphere. MTBE is expected to be highly mobile in soils and with likelihood of leaching into groundwater (USEPA, 1993a).

MTBE is not expected to persist in the atmosphere because of its rapid reaction with hydroxyl radicals, with a rate constant of 2.84 x 10^{-12} cm^3/molecule-sec at 25ºC (HSDB, 1994). Direct photolysis by UV absorption is not expected to be environmentally significant, given that MTBE does not absorb light of wavelength greater than 210 nm. Atmospheric half-lives of 3.0 days and 6.1 days have been calculated for polluted and non-polluted air respectively (USEPA, 1993a). Although leakages from underground storage tanks may be persistent, MTBE is expected to volatilize rapidly from soil surfaces. Also, limited evidence exists to support biodegradation under aerobic or anaerobic soil conditions (USEPA, 1993a). Low potential for bio-concentration has been indicated from the bio-concentration factors (BCF) of 1.5 and 1.4 reported for Japanese carp exposed to 10 to 80 mg/L MTBE and bio-concentration factors of 3.70 and 1.46 estimated from regression equations based on K_{OW} values (USEPA, 1993a).

2.4.7 Toxicology of MTBE

Upon entering the body through respiration, MTBE is changed into chemicals such as butyl-alcohol, methyl-alcohol, formaldehyde, formic acid, and carbon dioxide and these by-products leave the body by expiration or in the urine usually in 1 or 2 days (ASTDR, 1996). Acetone, tert-butyl-alcohol (TBA), methyl-alcohol, formaldehyde and carbon dioxide are the by-products if the MTBE exposure is by other routes (Jacobs *et al.*, 2000).

Animal studies have shown that MTBE is rapidly absorbed following oral or inhalation exposure, distributed in the blood to all parts of the body, including the brain and highest tissue levels were reported to occur in liver and kidneys. Acutely toxic oral doses can result in nervous system effects as well as muscular weakness and inflammation of the stomach and small intestines, as reported from experimental study of rodents with oral (lethal dose) LD_{50} values of 1.6-3.9 g/kg. Inhalation exposure resulted in inflammation of nasal mucosa and trachea. Similarly, blood chemistry changes and kidney abnormalities were observed in laboratory rodents exposed to high doses or concentrations of MTBE. However, limited information indicate that ambient levels of MTBE do not pose a health risk to healthy individuals, although susceptible population living under unique climatic condition such as sub-arctic may be adversely affected (USEPA, 1993a).

The potential carcinogenicity of MTBE in humans is unconfirmed as a result of limited information. However, it is classified by the US Environmental Protection Agency as a possible human carcinogen based on limited animal results of renal tubular cell tumors (adenomas and carcinomas) upon exposure to MTBE while varying the concentrations and exposure durations (Anderson, 1994; USEPA, 1993c).

Developmental, reproductive and neurotoxicity were observed in laboratory rodents exposed to high concentrations of MTBE, with limited information available on its potential effects on humans. Increase in maternal mortality, as well as significant reduction in mean pup weight throughout lactation was observed in laboratory two-generation study conducted on the same stain of rats (Anderson, 1994). Neurotoxicity effects reported from laboratory study of mice included blepharospasm, hypoactivity, ataxia, lack of startle reflex, stereotypy, and prostration (USEPA, 1993a).

MTBE is expected to show low acute toxicity to aquatic organism, although limited information is available and the lethal concentrations are generally greater than 100 mg/L. Same information constraints exist with toxicity to terrestrial organism, although the oral LD_{50} values of 1.6-3.9 g/kg for rats suggests that only when present at very high concentrations would the chemical be acutely toxic to terrestrial organisms. Also, according to the definition provided in the Federal Register (1992), MTBE is a volatile organic compound and as such can contribute to the formation of photochemical smog in the presence of other VOCs (USEPA, 1994).

2.4.8 Environmental Degradation

The reduction in concentration of MTBE in the environment can occur naturally or be enhanced by human interference. When in the atmosphere, MTBE may remain in its gaseous state until washed down by precipitation. The average lifetime in the atmosphere is 4 days, before degradation by reaction with hydroxyl radicals (OH·) or photolysis by penetration of ultraviolet (UV) light from the sun. Degradation by hydroxyl radicals results in the formation of tert-butyl-formate (TBF), methyl-acetate, acetone, TBA and formaldehyde; while degradation by photolysis results in carbon dioxide and water formation (Kinner, 2001).

2.5 Available Remediation Techniques for MTBE

Most available remediation techniques for MTBE are expensive due to its unique characteristics; high solubility, mobility and resistance to biodegradation (Kinner, 2001). Treatment efficiency depends on the MTBE concentration, properties of contaminated medium, such as aquifer permeability, alkalinity etc. Different remediation options are

currently available from surface and underground water contamination, including in-situ and ex-situ treatments. Air stripping, soil vapor extraction, phytoremediation, biodegradation, chemical oxidation, and adsorption techniques are promising options for MTBE removal from contaminated medium (Sutherland *et al.*, 2004).

2.5.1 Natural Attenuation

Depending on the natural processes to degrade and dissipate contaminants in soil and groundwater, this is a passive and cost-effective remedial approach. Mechanisms such as dispersion, sorption, volatilization, dilution, abiotic degradation and biodegradation are the biotic and abiotic types responsible for decrease in mass, toxicity, concentrations, volume and mobility of the contaminants. Although no direct human intervention is involved in this technique, long-term monitoring of the contaminant is usually required to protect residents and environment in down-gradient area. Hence, this technique is often considered to be monitored natural attenuation (USEPA, 2004). Some successful cases of MTBE natural attenuation have been reported making it a considerable remedial strategy, although the properties of MTBE may increase the difficulty of the use of this technique (Seagren and Becker, 2002). Natural attenuation may not be sufficient to protect aquifers and down-gradient receptors when MTBE biodegradation fails to contain the contaminant plume (Schirmer *et al.*, 1999).

2.5.2 Biodegradation

This is a microbial mediated process for the treatment of MTBE contaminated water resources. Biotransformation processes of MTBE are slow and isolation of degrading organisms is difficult, creating a problem with this remediation method. Several studies

have reported high stability of MTBE under anaerobic and aerobic conditions (Deeb *et al.,* 2000). There is little known about the biological fate of gasoline oxygenates, despite the established biodegradation research of many gasoline components.

Fujiwara *et al.,* (1984) reported the aerobic biodegradability of MTBE in sludge and soils, showing that 100 mg/L MTBE as degraded by activated sludge as measured by oxygen-uptake assay. Contrary to this observation, no biodegradation of MTBE at concentration of 10 mg/L after 60 days by microbes in aquifer soil, topsoil or activated sludge was reported in another research (Jensen and Arvin 1990). An aerobic mixed bacterial culture (BC-1), developed from microorganisms present in a chemical bio-treatment sludge capable of degrading MTBE was reportedly isolated in 1994 (Salanitro *et al.,* 1994). Anaerobic biodegradation of MTBE only in soil with lowest content of organic matter and pH around 5.5 was also reported (Yeh and Novak, 1994). MTBE degradation by methanogens in a contaminated site in North Carolina showed removal after 490 days following the removal of other gasoline components. The time requirement of this remediation technique makes it less favourable and might be considered only when the remediation is not critical (USEPA, 2000).

In a review of studies on biodegradation of MTBE, higher decomposition rates were reported under aerobic conditions (Diels and Lookman, 2007). MTBE biodegradation of 89% was reported in an in-situ case study in which oxygen curtain technology was employed (Induchny *et al*., 2005). The presence of ethylbenzene and xylene was reported to severely inhibit MTBE biodegradation. Similar result was obtained in another study where toluene and xylene were reported to significantly inhibit MTBE biodegradation, while less inhibitory behaviour was reported with TBA and ethylbenzene (Wang and

Deshusses, 2007). Muller *et al.*, (2007) reported environmental conditions to be responsible for relatively slow field MTBE biodegradation.

2.5.3 Air Stripping

In the treatment of groundwater contaminated with volatile organic compound, air stripping is a well-established process, with several successful applications in municipal wastewater treatment (Melin, 2000). When compared to benzene, 2 to 5 times more air is required for treatment of same amount of MTBE contaminated water with below 5 µg/L concentration (USEPA, 1998). This is an ex-situ (pump and treat) remediation technique for groundwater sources contaminated with MTBE. Given the solubility and hydrophilic properties of MTBE pump and treat techniques are considered effective in its remediation. Air stripping involves the use of inert gas for MTBE removal from contaminated water sources. This technique is not economically feasible because MTBE has affinity for aqueous phase than gaseous phase.

Another important consideration with air stripping is that it transfers MTBE from one phase to another; therefore further treatment of the gaseous phase is required. Keller *et al.*, (1999) reported that heating the contaminated water as well as reduction in overall pressure of air stripping system improves the effectiveness of MTBE removal by this technique, due to increase in the Henry's constant. Air stripping has been reported by some researchers as non-economical for treatment of MTBE contaminated water sources (Hassen and Gross, 2000). Removal efficiencies of more than 90% were reported in a study on the application of air stripping for treatment of MTBE contaminated drinking

water, with air stripping mostly combined with other treatment methods such as adsorption with activated carbon in most studies (Deeb *et al.,* 2006).

2.5.4 Chemical Oxidation

This involves the use of oxidizing agents such chlorine, hydrogen peroxide (H_2O_2), ozone (O_3), Fenton reagent (H_2O_2 and Fe(II)). Yielding low concentrations of TBA and acetone as degradation by-products, Fenton reagent is considered to be the most effective oxidation treatment and affected by pH, alkalinity and aquifer permeability (Jacobs *et al.,* 2000). Damm *et al.,* (2002) reported electron exchange, hydrogen atom abstraction and direct oxygen donation as the reaction mechanism of potassium permanganate, in a study of oxidation of MTBE. Fast degradation of MTBE was reported in a study with bi-functional aluminum obtained by sulphating aluminum with sulphuric acid. TBF, TBA, methyl acetate and acetone were the by-products from the treatment process (Lien and Zhang, 2002).

2.5.5 Advanced Oxidation Processes (AOPs)

These remediation processes depend on the generation of hydroxyl radicals, which are considered to be powerful oxidant, removing contaminants from aqueous phase while producing less harmful by-products. A combination of different techniques such as ultraviolet radiation (UV), ozone (O_3), hydrogen peroxide, photo-Fenton (Fe^{2+}) and titanium dioxide (TiO_2) are the major AOP techniques used for different drinking water treatments (USEPA, 1999). The major challenge with the use of AOP for MTBE remediation is the degradation by-products, most of which are not degradable by the same process. TBF, TBA, acetone, methanol and formaldehyde are the common by-products from the remediation process (Chang and Young, 2000).

2.5.5.1 Photocatalysis

This process is based on the use of semiconductor material as a catalyst, based on heterogeneous process with high oxidation potential (Pirkanniemi and Sillanpaa, 2002). Titanium dioxide (TiO_2) is one of the semiconductor materials that has been most studied and used in this oxidation process because of it high degradation efficiency, minimal toxicity and stability in treatment of polluted water. Barreto *et al.,* (1995) reported a successful degradation of MTBE of 1mM initial concentration using UV irradiation (medium pressure mercury lamp) and TiO_2 as catalyst. The primary degradation by-products from this study were TBA and TBF, which were subsequently degraded but at slower rate compared to MTBE. A similar study by Hu *et al.,* (2008) reported approximately 98% removal of MTBE with initial concentration of 0.1 mM. The removal efficiency was observed to decrease with increase in initial concentration and TBA was the major intermediate product generated, which was eventually mineralized. Nanoparticles of ZnO as alternative to TiO_2 in photo-catalytic degradation of MTBE was studied by Eslami *et al.,* (2008), reported to follow fist-order reaction kinetics at pH 7 and rate constants reported to be 0.183-0.022 min^{-1} for initial MTBE concentrations from 10-500 mg/L respectively.

2.5.5.2 Ozone/Hydrogen Peroxide

This AOP involves the use of hydrogen peroxide (H_2O_2) in conjunction with ozone (O_3) for enhancement of hydroxyl radicals (·OH) formation. Hydroxyl radical is an oxidant established to be stronger than sole use of molecular ozone. Economic benefit is considered the principal motivation for application of O_3/H_2O_2 as compared to the use of

molecules of either alone. Mitani *et al.,* (2002) reported ozone alone to be 5 times less efficient than O_3/H_2O_2 for removal of MTBE in water. The inability of turbidity and iron/nitrate content to significantly affect the efficiency of O_3/H_2O_2 is considered another important advantage (Melin, 2000). However, the major drawback of this AOP is the formation of hazardous bromate during MTBE degradation (Shih *et al.*, 2003). Mitani *et al.,* (2002) reported similar MTBE degradation pathways for O_3/H_2O_2 and application of ozone alone, with difference in proportion of by-products.

2.5.5.3 UV/Ozone

Baus *et al.,* (2007) reported the combination of UV and ozone in treatment of MTBE contaminated water to be more efficient than the application of either UV or ozone alone. The combination was reported to result in maximum per oxidant yield of hydroxyl radical (·OH). In treatment of MTBE contaminated water with relative turbidity, UV/ozone was reported to be two times faster than the use of ozone alone (Graham *et al.,* 2004). However, intensive cost and energy requirements of this AOP are considered the major drawbacks of UV/ozone combination in MTBE treatment (Melin, 2000). In a study on the application of UV/ozone for treatment of MTBE contaminated water with initial concentration of 10 mg/L, removal efficiency greater than 99.9% was reported. Although, TBF as a main by-product was reported in large amounts (Chang and Young, 2000).

2.5.5.4 UV/Hydrogen Peroxide

This AOP involves a conjunction between UV and hydrogen peroxide (H_2O_2), which plays dual role of disinfection with UV irradiation and degradation of organic contaminants by hydroxyl radicals (·OH). Degradation of a broad range of organic

contaminants by the generated hydroxyl radicals and minimal bromate formation are principal benefits of UV/H_2O_2 over traditional oxidants such as ozone (Vilhunen *et al.,* 2011). Georgi and Kopinke, (2005) reported that lowering the pH by acidification is a major requirement of using Fenton reagent for MTBE removal, which results in sample contamination with dissolved iron. A challenge not encountered when H_2O_2 is combined with O_3 or UV. However, the decomposition of H_2O_2 into oxygen and water without producing any toxic compound makes it environmentally friendly and is considered a major advantage for its use (Burbano *et al.,* 2005).

2.5.5.5 Fenton process (Fe (II) + H_2O_2)

This AOP also involves the formation of hydroxyl radicals for the degradation of contaminants through addition of H_2O_2 to Fe^{2+} salts. This process is considered relatively simple for ·OH generation without requiring special apparatus or reactants (Pirkanniemi *et al.,* 2007). The non-toxic nature and abundance of iron, coupled with the handling ease and environmental friendliness of hydrogen peroxide make this reactant attractive in oxidation process. Other advantages of Fenton over other AOPs are its relatively much less energy requirement and absence of vapour emissions, hence not requiring off-gas treatment. However, the need for pH adjustment pre and post-treatment along with need for iron removal are the major drawbacks of this AOP (Melin, 2000).

Neppolian *et al.,* (2002) reported a combination of Ultrasound (US) and Fe/H_2O_2 as being more effective than the use US alone, producing TBF and acetone as by-products. Similar study showed higher degradation rate using H_2O_2 and TiO_2, generating TBF, TBA and acetone as by-products, while no TBF detected with the use of US alone (Bertelli and

Selli, 2004). The breakdown of water in hydrogen peroxide, hydrogen radicals and ozone by radiolysis using alpha radiation was applied for the degradation of MTBE and TBF, TBA, acetone and methyl acetate were by-products reported in the study (Hsieh *et al.*, 2004). A combination of ozone and hydrogen peroxide reportedly gave better degradation of MTBE, with visible reduction observed at high initial concentration of O_3 and H_2O_2. However, the complete degradation was only observed when the water quality standard for bromate was exceeded, which is a disadvantage to this technique (Burbano *et al.*, 2005).

2.5.6 Adsorption

Adsorption is one of the promising techniques for the removal of synthetic organic compounds from many contaminated environmental media, with broad applications (Weber *et al.,* 1991). Having tested successfully for the removal of MTBE from contaminated water, Granular Activated Carbon (GAC) is the most popularly used adsorbent (Shih *et al.,* 2003; Sutherland *et al.,* 2004). However, a challenge with this technique is the poor removal efficiency that may be observed especially when other synthetic organic compounds co-exist with MTBE, rendering the carbon adsorption process less cost-effective for MTBE removal (Hung and Lin, 2006). Another constraint is that the presence of natural organic matter may slow the adsorption kinetics and reduce the adsorption capacity while applying activated carbon in natural water (Sontheimer *et al.*, 1988).

2.5.6.1 Granular Activated Carbon

On the subject of water and wastewater treatment, one of the most commonly used adsorbents is activated carbon, generally considered a universal adsorbent. Broad study

has been conducted on the application of granular activated carbon (GAC) for adsorption of MTBE from contaminated water and waste water systems (Rossner and Knappe, 2008). The GAC system is considered beneficial because the methods and equipment are well established, its simplicity, absence of off-gas treatment and commercial availability. In order to achieve a full scale operation of GAC systems, disinfection, pH adjustment, filtration and precipitation are required as pre-treatment activities (Melin, 2000).

Inal *et al.,* (2009) studied the application of activated carbon (Norti GAC 1240) commercially available for the adsorption of MTBE and ETBE. The outcome of this study showed that adsorption of MTBE increased with increase in its initial concentration from 2 to 15 mg/L, while the adsorbent dosage for the study was constant at 8 g/L. The optimum adsorption was also attained after 15 hours of contact. At an equilibrium solution concentration of 1 mg/L for MTBE, the adsorption capacity was estimated as 5.5 mg/g. In a similar study using GAC from Shanghai Activated Carbon Corporation, China, GAC dosage of 1 g/L reported a maximum adsorption capacity of 204 mg/g (Chen *et al.,* 2010).

A separate study focused on the role of surface chemistry and pore morphology on MTBE adsorption using GAC was conducted. Results from this study showed micropores with width range of 8-11A to be more efficient for MTBE adsorption. MTBE removal was also found to be more efficient upon application of hydrophobic adsorbents than with their hydrophilic counterparts (Li *et al.,* 2002). The presence NOM in the treated water has been reported to result in a drop in the MTBE removal efficiency using GAC. Competition for adsorption sites, preloading with NOM and pores clogging are potential causes of reduction in GAC adsorption efficiency in the presence of NOM (Melin, 2000).

Regeneration, using chemical or thermal procedures may be used to recover spent GAC and re-establish its sorption capacity. A number of studies on possible change in sorption capacity following regeneration have shown that no loss of sorption capacity resulted post regeneration. Despite this wide use of the GAC for MTBE removal from water, limited information still exist concerning the system (Melin, 2000).

2.5.6.2 Zeolites

Commonly used for removal of contaminants from water and wastewater, zeolites are microporous minerals, mainly composed of aluminium and silicon. The features which make zeolite of particular scientific importance as an adsorbent are its stability over a broad range of environmental conditions such as pH or temperature and selective sorption capacity (Anderson, 2000). The chemical composition and pore size are the main parameters promoting the sorption capacity of zeolite (Arletti *et al.,* 2012). When compared to coconut-shell based GAC, silicate-zeolite in a study showed higher capacity for MTBE adsorption (Rossner and Knappe, 2008). In a related study, the presence of NOM in the aqueous solution did not alter the adsorption efficiency of silicate-zeolite as was observed with GAC. The useful life of GAC was estimated to be approximately 5 times less than silicate zeolite. Also, no competition for active adsorption sites on mordenite zeolite was observed in a study on NOM and MTBE, with the large size of the NOM attributed to its inability to bind to the active sites on the zeolite material (Hung and Lin, 2006). In a study on MTBE adsorption by mordenite zeolite, 75% removal efficiency was reported (Arletti *et al.,* 2012). Surface modification of zeolite has been reported to enhance its MTBE sorption efficiency. Ghadiri *et al.,* (2010) reported improvement in MTBE sorption using hexadecyltrimethylammonium chloride (HDTMA)

modified zeolite, with removal efficiency of about 80% reported from the study. In the same study, the role of pH of the solution was investigated and results showed increase in MTBE removal efficiency with decrease in solution pH. This observation was attributed to the adsorbent's weak positive charges which tends to be maximum in acidic environment.

2.5.6.3 Ion Exchange Resins

Resins are synthetic materials available as alternative to the use of GAC and zeolite in adsorption environmental applications. Carbonaceous resins produced from partial pyrolysis of beads of macroporous polymer and polymeric resins produced from polymerization in inert conditions are the two main groups of wide application. A major advantage of resins over GAC for sorption application is the ability to control its pores size distribution (Melin, 2000). However, the relatively high cost associated with use of resin over traditional adsorbents has limited its application despite other obvious benefits. Similar to observation with GAC, the presence of NOM in the solution was reported to bring about reduction in the MTBE adsorption efficiency of resins, as a result of competition for active adsorption sites (Davis and Powers, 2000). Solvent impregnated was also reported to bring about improvement in the MTBE removal efficiency of resins. In a study on the impact of solvent impregnation, impregnation of MPP resin was reported to increase its MTBE removal efficiency 3 times more than its un-impregnated counterpart (Burghoff *et al.*, 2010).

2.5.6.4 Other Adsorbents

In addition to the established adsorbents of MTBE from aqueous solutions, several other forms of adsorbent materials, whether naturally occurring or synthesized are being

studied for their MTBE adsorption efficiencies. Sim *et al.,* (2009) reported the application of different clay minerals for the adsorption of MTBE. The concentration of humic acid was a major factor reported as affecting the MTBE adsorption efficiency of the minerals studied. In another study, application of raw and thermally modified diatomite was carried out, in which thermal modification was reported to improve the sorption efficiency of the diatomite. However, the efficiency was observed to be 20 times lower that the sorption efficiency of activated carbon (Aivalioti *et al.,* 2012a). Li *et al.,* (2012) reported on the application of modified oil sludge (MOS) for removal of MTBE from water. A removal efficiency of 88-93% was reported, as well as a desorption rate of 10%.

2.5.6.5 Fly Ash Adsorption

Scientific studies into the use of readily available low cost materials for the removal of environmental contaminants such as heavy metals and other organic pollutants have gained significant attention. Fly ash constitute the major particulate waste by-product during the generation of electricity by burning of coal or heavy liquid fuel. Generated as a non-combustible, fine residue, carried in the flue gas and usually collected with the aid of electrostatic precipitators, and having a uniform size distribution of particles ranging 1 to 10 mirometers. Presently, the major applications of fly ash are in soil stabilization and as additives in the manufacturing of cements, with a large proportion of the fly ash material being disposed by land filling. The potential for utilizing fly ash as an inexpensive adsorbent was driven by its high alumina and silica content, where it could be adopted as liner for landfills to minimize leachate of organic pollutants (Mott and Weber, 1992).

In a batch adsorption study, comparison of the adsorption effectiveness of fly ash and activated charcoal for mono-chlorinated phenols removal in contaminated waters were examined, where although activated charcoal exhibited a much higher adsorption capacity, fly ash showed potential as an inexpensive adsorbent with an intermediate adsorption capacity (Aksu and Yener, 2001). Laohaprapanon *et al.,* (2010) reported wood fly ash as alternative low-cost sorption media for removal of organic compounds from wastewater, following results from study which showed reductions of chemical oxygen demand, biological oxygen demand and total organic carbon by approximately 37, 24 and 30% respectively. The physicochemical characteristics of nitric-acid-activated fly ash were reported to be better than those of raw fly ash in a study for the removal of p-nitrophenol from water, with highest removal rate of 98% being reported at pH 2.0 and pH 5.1 (Zhang *et al.,* 2012).

In an experiment to access the adsorption of phenolic compounds by fly ash, phenol, 3-chlorophenol and 2,4-dichlorophenol were studied for their affinities for fly ash and phenol displayed the highest affinity as compared to the other phenolic compounds. Although, unfavourable isotherms were reported for all the contaminants studied (Akgerman and Zardkoohi, 1996). In another study on fly ash application for the removal of lead ions from aqueous solution, given lead being widely used in batteries with established toxicity properties. The removal efficiency was noted to be maximum at pH range of 4 to 6 and the maximum adsorption obtained was 91.89% removal of lead ions (Yadla *et al.,* 2012). Phosphate which is associated with eutrophication and several other secondary problems in contaminated aquatic environment was studied for potential application of fly ash in its removal from aqueous solution. In this study, optimum

removal of phosphate using fly ash was obtained at a pH of 7 and a percentage removal of 95% was attained in the batch experimental condition (Ragheb, 2013).

Given the difficulties associated with the treatment of a number of environmental contaminants, the combination of fly ash with other established remediation agents has similarly attracted growing attention. A combination of fly ash and photo-fenton (Fe^{2+}/H_2O_2) was studied for the removal of cadmium (heavy metal) and methyl-orange (dye) from aqueous solution. In this study, removal efficiencies of up to 70% was reported for the dye, and up to 88% for the heavy metal (Visa and Duta, 2013a). A similar study was conducted for the removal of heavy metals and surfactants, using a combination of fly ash and titanium oxide. In this study, cadmium and cupper ions were studied as the choice metals, while 1-hexadecyltrimetylammonium bromide – HTAB and dodecylbenzenesulfonate – SDBS were the surfactants of interest. Parallel adsorption of heavy metals and surfactants was reported from the study, with efficient removal to obtain water in compliance with discharge regulations (Visa and Duta, 2013b).

The efficiency of fly ash (raw or modified) for MTBE adsorption is unknown. Hence, fly ash is considered a potentially simple and economic solution for the removal of MTBE in contaminated water sources, which was the core of this study.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Chemicals

The MTBE used in this study was purchased from Sigma-Aldrich, Saudi Arabia, with 99.999% purity (HPLC grade). Deionized water from Mili-Q direct purification system was used for preparation of 100mg/L MTBE stock solutions, from which the water was spiked prior to treatment. Aluminum nitrate [$Al(NO_3)_3.9H_2O$] from Fisher Scientific Company (98% purity), ferric nitrate [$Fe(NO_3).\ 9H_2O$] from LOBA Chemic PVT Ltd (71% purity) and silver nitrate ($AgNO_3$) from Eurostar Scientific Ltd were used as sources of aluminum, iron and silver respectively. Ethanol from Sigma Aldrich with 99.8% purity was used for adsorbent modifications.

3.2 Preparation of Fly Ash Materials

The fly ash used in this study was obtained from Saudi Aramco, where its collection is done via the use of electrostatic precipitators during the combustion of heavy liquid fuel, from the local electricity plant. Based on the experimental design, three (3) broad categories of the fly ash materials were used in this study, namely; raw fly ash, acid treated fly ash and metal oxide impregnated fly ash.

3.2.1 Preparation of Raw Fly Ash (non-modified fly ash)

In this process, a weighed amount of the fly ash material was soaked in deionized water inside a beaker and was stirred on magnetic stirrer at a speed of 150rpm for 2 hours. Following the stirring, the mixture was allowed to settle for 10 minutes, before the water was decanted and the process was repeated 5 times. After washing, slurry phase was dried inside the oven at temperature of 80^{o}C for 12 hours, and stored until used for the batch treatment experiments.

3.2.2 Preparation of Acid Treated Fly Ash (non-modified fly ash)

In this task, some amount of the washed and dried raw fly ash material were weighed and nitric acid was added in the volume ratio of 1:3 (ash : nitric acid). The mixture was stirred at a temperature of 120^{o}C for 24 hours, with a condenser attached. Following stirring, the mixture was allowed to stand for 2 hours for segregation of phases, after which the acid was decanted and the slurry phase was washed with deionized water. The washing was done repeatedly until the pH of the waste water matched that of the original deionized water used for the washing activity. After washing, the slurry phase was dried inside the oven at temperature of 100^{o}C for 12 hours, and stored until used for the batch treatment experiments.

3.2.3 Preparation of Impregnated Fly Ash (modified fly ash)

The fly ash impregnation involved doping oxides of aluminum, iron and silver onto the acid treated fly ash material. For each of the metal oxide, 10% metal (by mass) was impregnated unto the fly ash material. In the preparation, appropriate weights of the aluminum nitrate [$Al(NO_3)_3.9H_2O$], ferric nitrate [$Fe(NO_3).9H_2O$] and silver nitrate

($AgNO_3$) were used as sources of aluminum, iron and silver respectively. Acid treated fly ash material of appropriate weight to make 90% (by mass) was added and the mixture soaked in pure ethanol. The mixture was subjected to sonication for 30 minutes, before calcination at 350^oC for 3 hours, and then stored until used for the batch treatment experiments (Fierro, 2005). Aluminum hydroxide was also prepared and utilized in this study. In the preparation of the aluminum hydroxide coated fly ash, aluminum sulphate [$Al_2(SO_4)_3.16H_2O$] and sodium hydroxide were utilized. 200 mL of 0.6 M aluminum salt was stirred in the beaker, followed by gradual addition of 20 grams of acid treated fly ash and stirred till the fly ash was completely soaked in the salt solution. Afterwards, 3.0 M sodium hydroxide (5 times concentration of aluminum salt) was gradually added to the mixture and stirred at 180 to 200rpm. The addition of sodium hydroxide was stopped when the pH of the solution reached the desired value of 5-7. The slurry mixture was then filtered using a vacuum filter and dried in the oven at temperature of 110^oC. The resultant aluminum hydroxide coated fly ash was then washed several times to remove the sodium sulphate salt, and then dried at 100^oC for 4 hours, and stored until used for batch treatment experiments.

3.3 Characterization of Fly Ash Powder (modified and non-modified)

In order to understand the surface morphology, microstructure and other physical and chemical properties of the adsorbent materials, a number of instrumental studies were conducted on the prepared materials.

3.3.1 Brunauer-Emmett-Teller (BET) Surface Area Analysis

BET analysis was conducted for the adsorbent materials at the three (3) forms of preparation to understand their precise surface area. This encompasses external area and pore area (m^2/g) by multilayer nitrogen adsorption measured as a function of relative pressure, using a fully automated analyzer. This involved physical adsorption of gas (nitrogen) on the adsorbent's surface and subsequent calculation of the amount of trapped gas on the surface of the adsorbent equivalent to a monomolecular layer. The van der Waals forces were responsible for the physical adsorption of the gas on the adsorbent material. Prior to determination of the specific surface area of the adsorbent, gases or vapours which might have been adsorbed during generation, treatment, storage or handling of the adsorbents are removed by outgassing. Failure to carry out outgassing prior to determining the specific surface area will result in reduction of its value. This outgassing was achieved through the application of a vacuum. It involved purging the adsorbent in flowing steam of dry, non-reactive gas coupled with application of adsorption-desorption cycling method.

3.3.2 Thermo-Gravimetric Analysis (TGA)

Following preparation of the adsorbent materials, TGA was performed to evaluate accuracy of process based on weight percentage determination. SDT Q600 TGA unit was utilized for this work, 7 – 10 mg of adsorbent materials were used, with an alumina pan, a dynamic temperature ramped at 10^oC per minute to 800^oC and air as the flow gas with a flow rate of 100 mL per minute.

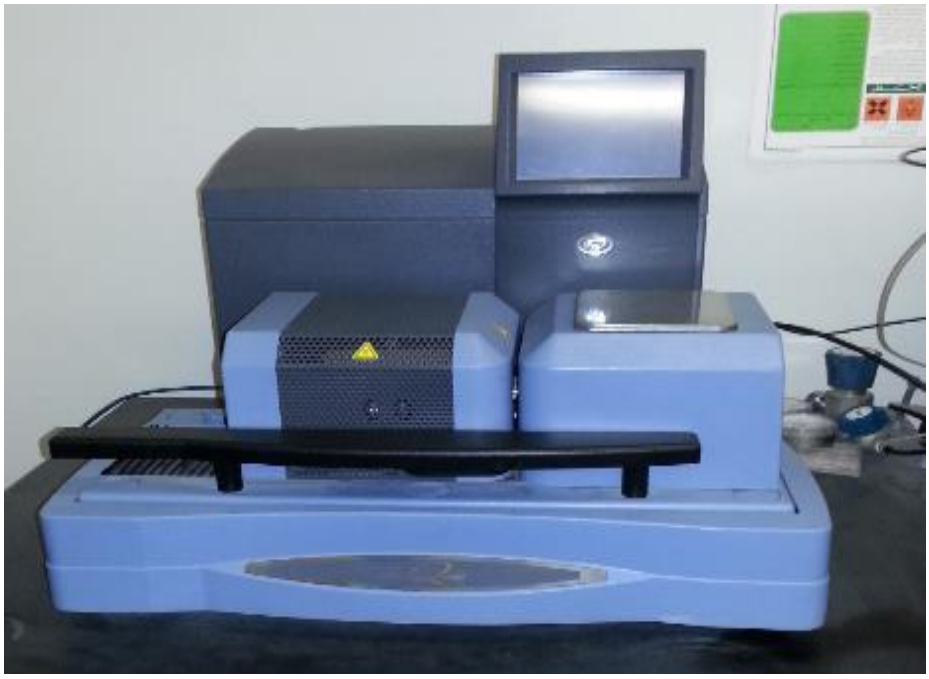


Figure 3.1: Thermo-gravimetric analyzer used in characterization

3.3.3 Field Emission Scanning Electron Microscopy (FESEM)

To further understand the surface morphology and adsorption potential of the materials, the prepared materials were subjected to field-emission scanning electron microscopy. SEM (JOEL JSM 5900LV) was used for the surface morphology analysis. To bring about reduction in charging effect, a thin layer of gold was used to sputter the samples, with low voltage back scattered electron (BSE) and secondary electron (SE) imaging being carried out. Directly above the sample and below the objective pole-piece was the high contrast BSE detector mounted, to achieve high resolution micrographs at low kilo voltages (kV). The choice of FESEM was because it produces less electrostatically distorted clearer images with resolution as low as 1.5 nm. This images are considered to be 3 to 6 times preferable to the conventional type. The fine surface morphology of the adsorbent nanoparticles was cable of being observed with the energy filter coupled to the microscopy unit. Reduction of incident electron charging and penetration of the sample

was achieved with the aid of the Gentle Beam (GB) mode, which was responsible for decelerating the incident electron prior to its contact with the sample. An important observation from this method is the preservation of the sample's integrity, such that its surface was not damaged, while the high quality resolution of the images were achieved.

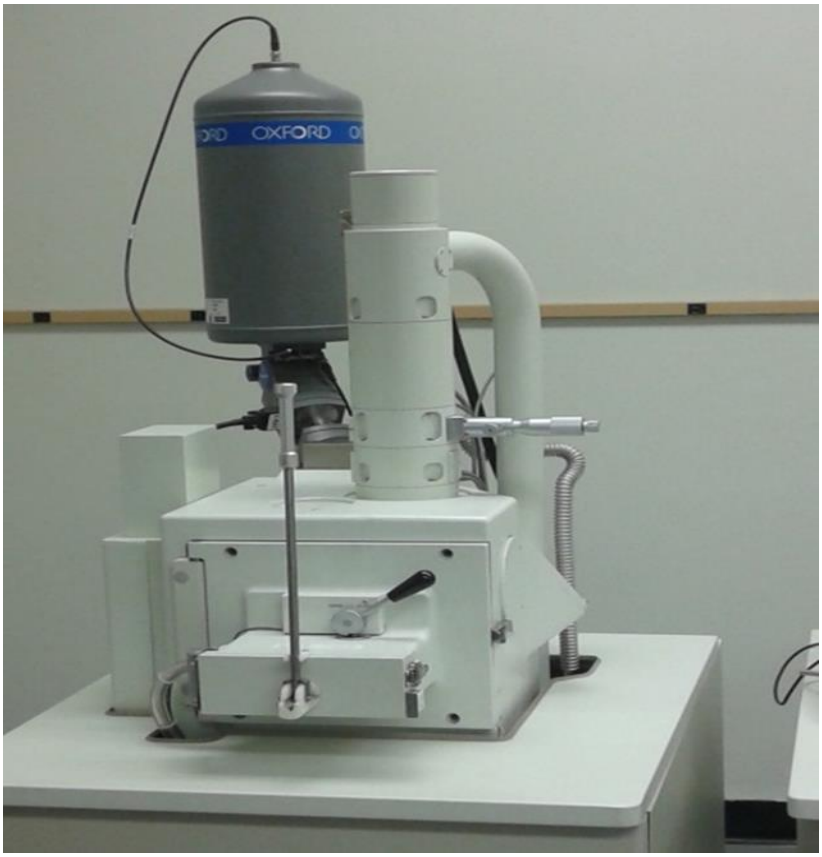


Figure 3.2: SEM (JOEL JSM 5900LV)

3.3.4 Energy Dispersive X-ray Analysis (EDX)

The EDX was employed to determine the elemental composition of the prepared adsorbent materials. In this study, an EDX detector attached to the FESEM unit was simply employed for this purpose. The SEM coupled with EDX (JSM 5800LV) was used in this study. A thin polymer window was responsible for separation of this x-ray detector from the SEM chamber. The detected x-ray's energy was determined by a pulse processing circuitry and the x-ray data was interpreted by an analyzer equipment prior to

display on the computer screen. When the sample was exposed to electrons of minimum kinetic energy, characteristic x-rays can be generated from it. This involves excitation of atoms in the sample by the incident electrons and during relaxation of the atoms, transition of electrons from outer to inner electron shells result in the release of energy as photons. The x-ray detector is a lithium doped silicon semiconductor. The striking of the semiconductor by the x-ray generated electrical charges, which were then analyzed to determine the number of x-rays emitted and their associated energy. This energy emissions were then used as finger prints of the elemental composition of the samples of adsorbent materials.

Figure 3.3: SEM – EDX (JSM 5800LV)

3.4 Treatment of MTBE-Spiked Water

Deionized water was spiked with MTBE and was subsequently treated on a bench scale, using various dosages of the fly ash materials prepared and characterized.

3.4.1 Preparation of MTBE Aqueous Solution

The stock MTBE solution used for this study was prepared from 99.999% purity (HPLC grade) MTBE standard solution purchased from Sigma-Aldrich. Deionized water from Mili-Q direct water purification system was used for dilution of the stock solution to the desired concentrations used in the batch experiments. The preparation process involved mixing appropriate volumes of the MTBE with deionized water solution and stirring for 2 hours to ensure dissolution of the MTBE in water (May *et al.*, 2003).

3.4.2 Batch MTBE Treatment Experiments

A variety of pre-designed experiments were carried out using 100 mL of MTBE spiked deionized water. For each of the batch set up, different weights of the adsorbent material were added to the 100 mL spiked water containing pre-determined concentration of MTBE and tightly sealed, to avoid loss by volatilization. The flasks were then placed on the conical flask shaker at temperature of 25 ± 3^{o}C, while altering the experimental parameters, which included the agitation speed (50 – 200rpm), dosage of the adsorbent (10 – 100 mg), contact time of the adsorbent (1 – 5 hours), initial pH of solution (3 – 9), initial concentration of MTBE (500 – 1000 µg/L) and the type of adsorbent (raw fly ash; acid treated fly ash; impregnated fly ash with oxides of aluminum, iron and silver; aluminum hydroxide coated fly ash). Following agitation for a desired duration of time, the mixture was allowed to stand for 10minutes for settling of adsorbents, after which

1mL of sample was collected from the supernatant into a clean glass vial and analyzed using the GC/MS unit. For each of the batch experiments, blank runs were conducted to determine loss to the container/environment, duplicate samples were also collected and analyzed as a form of quality control to ensure accuracy of experimental results.

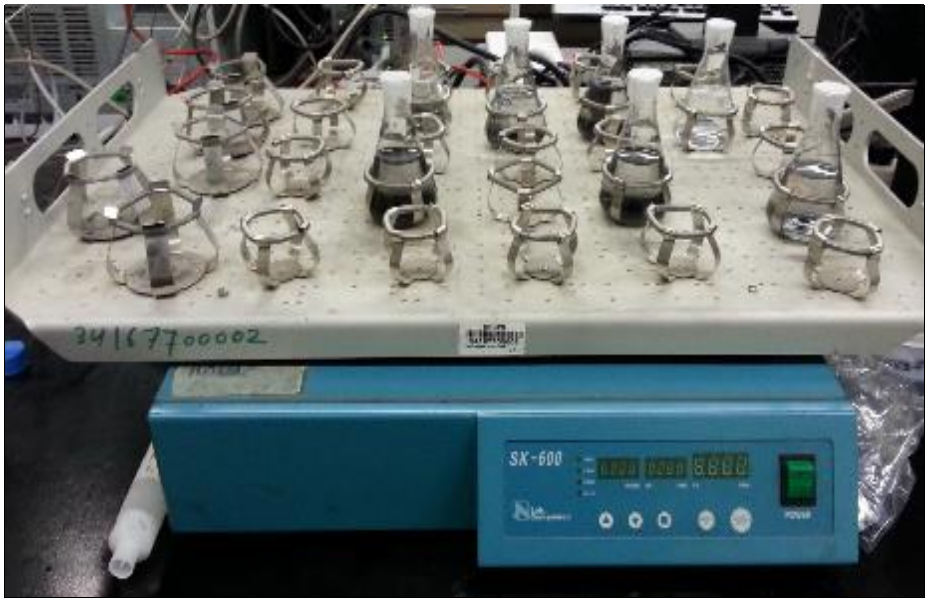


Figure 3.4: Mechanical shaker used for batch experiments

3.4.3 Sample Instrumental Analysis

Following preparation of the stock solutions, the Thermo Scientific Trace GC Ultra gas chromatography / mass spectrometry (GC-MS) unit was calibrated to cover the range of concentrations to be used in the batch experiments (0.5 to 5,000 µg/L). For all of the concentration analyses, 1.0 mL of the solution was collected in a glass vial, and analyzed. The ISQ single quadrupole mass spectrometer coupled thermo scientific trace gas chromatography unit, fitted with a Tiplus headspace injector unit and an auto-sampler was used for the analysis of the MTBE concentrations in the samples collected during the batch experiments. A DB 520.2 fused silica capillary gas chromatography column was

used in the unit (60 m – length; 0.32 mm – internal diameter and 1.80 µm thickness). The stationary phase used was diphenylidmethyl polysiloxane, while the carrier gas was helium, at a constant flow rate of 1.7 mL/min.

Figure 3.5: Thermo Scientific Trace GC ultra GC-MS

The instrument configuration was programmed at temperature of 50^{o}C for 1 minute, ramped to 220^{o}C at rate of 20^{o}C/min and held for 1 minute. In order to volatilize the target analyte, incubation of the sample bearing vials occurred at temperature of 80^{o}C for 5 minutes in the auto-sampler, before the volatilized contents are taken by the syringe and injected into the unit. The electron ionization mode was utilized for the mass spectrometry unit (detector), having mass transfer line temperature of 200^{o}C and ion source temperature of 200^{o}C. Selected ion monitoring (SIM) mode was used to obtain the ion current at the mass to charge ratio of interest, having set the mass range at 72.50 – 73.50 for MTBE.

The amount of MTBE adsorbed per gram of adsorbent material (q_e) was given as;

$$q_e = \frac{\mathrm{V}}{m}\,(C_O - C_\mathrm{e}) \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad (1)$$

Also, the percentage removal (R) was calculated using the equation below;

$$\%R = \frac{C_O - C_\mathrm{e}}{C_O} \times 100 \; - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad (2)$$

From the equations above, C_o and C_e are the initial and equilibrium MTBE concentrations respectively (mg/L), V is the volume of the MTBE spiked aqueous solution (L), and m is the mass of the adsorbent material (g).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Characterization of Adsorbent Materials

Following preparation of the adsorbent materials, instrumental characterization was performed to understand their microstructure, surface morphology, elemental composition and accuracy of impregnation process. These observations were subsequently correlated to the adsorption behaviors of the materials. The results obtained from a variety of relevant instrumental study of the adsorbent materials, also enhanced our understanding of the mechanism of MTBE removal from the solution.

4.1.1 Brunauer-Emmett-Teller (BET) Surface Area Analysis

The total specific surface area in m^2/g of the adsorbent materials, which encompassed the external and pore areas were obtained, providing information to understand effects of surface porosity and particle size on the adsorption application. From Table 4.1, it was noted that the fly ash material had a higher surface area value in its raw state than what was determined following acid treatment, due to the presence of metals and other impurities attached to it upon collection from the plant during the liquid fuel combustion process. The removal of these impurities resulted in the drop in its surface area after acid treatment. Following impregnation with the different metal oxides used in this study, a significant improvement was recorded in the surface area of the impregnated fly ash. This increase in surface area being due to improved distribution of the metal oxide

nanoparticles on the surface of the fly ash materials. The activated carbon used in this study was also subjected to surface area analysis, and contrary to the observation with fly ash, metal oxide impregnation resulted in a decrease in the surface area of the activated carbon. The Nanotrack particle size analysis showed the average particle size to be 4470 nm and 2880 nm for raw fly ash and acid treated fly ash respectively.

4.1.2 Thermo-Gravimetric Analysis (TGA)

The elemental composition of the adsorbent materials were indicated by the percentage weight loss obtained from the TGA. From Figure 4.1, it can be observed that upon total burning of the fly ash material, there was residual material which was not burned at the set temperature. This was a further confirmation of the existence of other substances (impurities) attached to the fly ash material from the combustion of heavy liquid fuel during electricity generation at the plant. However, Figure 4.2 shows a complete burning of the adsorbent material following acid treatment, indicating the removal of the impurities attached to the fly ash material. From Figures 4.3 to 4.5, it can be observed that approximately 10% of the adsorbent material was not burnt at the temperature set for the TGA. This was due of the impregnation of the acid treated fly ash with metal oxide, which were also seen as colored residues in the alumina pan after the analysis (white residue for silver oxide and aluminum oxide impregnated fly ash and reddish brown for ferric oxide impregnated fly ash). Also, for the three metal oxide impregnations, 90% (by weight) of fly ash was used in the preparation of the adsorbents, and approximately 80% (by weight) was recovered after calcination, as seen from the residual following weight loss. This indicated that a significant proportion of the fly ash material (approximately 89%) was recovered following the metal oxide impregnation.

Table 4.1: Brunauer-Emmett-Teller (BET) Surface Area Analysis of adsorbent materials

ADSORBENT	BET SURFACE AREA (m^2/g)
Raw fly ash	7.1539
Acid treated fly ash	6.0245
Ferric oxide impregnated fly ash	9.0565
Aluminum oxide impregnated fly ash	11.8890
Silver oxide impregnated fly ash	16.7890
Activated carbon	1,126.6314
Silver oxide impregnated activated carbon	1,039.477

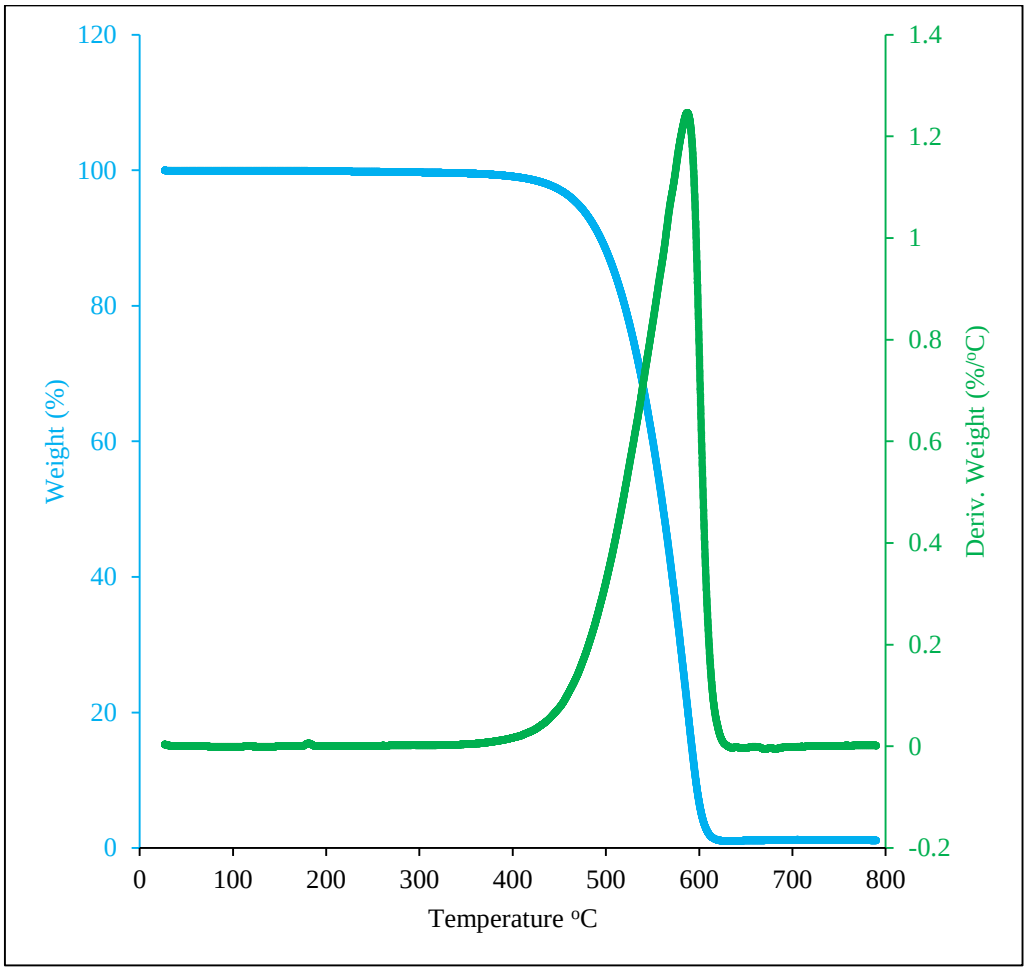


Figure 4.1: Thermo-gravimetric analysis result for raw fly ash from 7.138 mg raw fly ash, in alumina pan, temperature ramp 10°C/min to 800°C and air as flow gas with a flow rate of 100 mL/min.

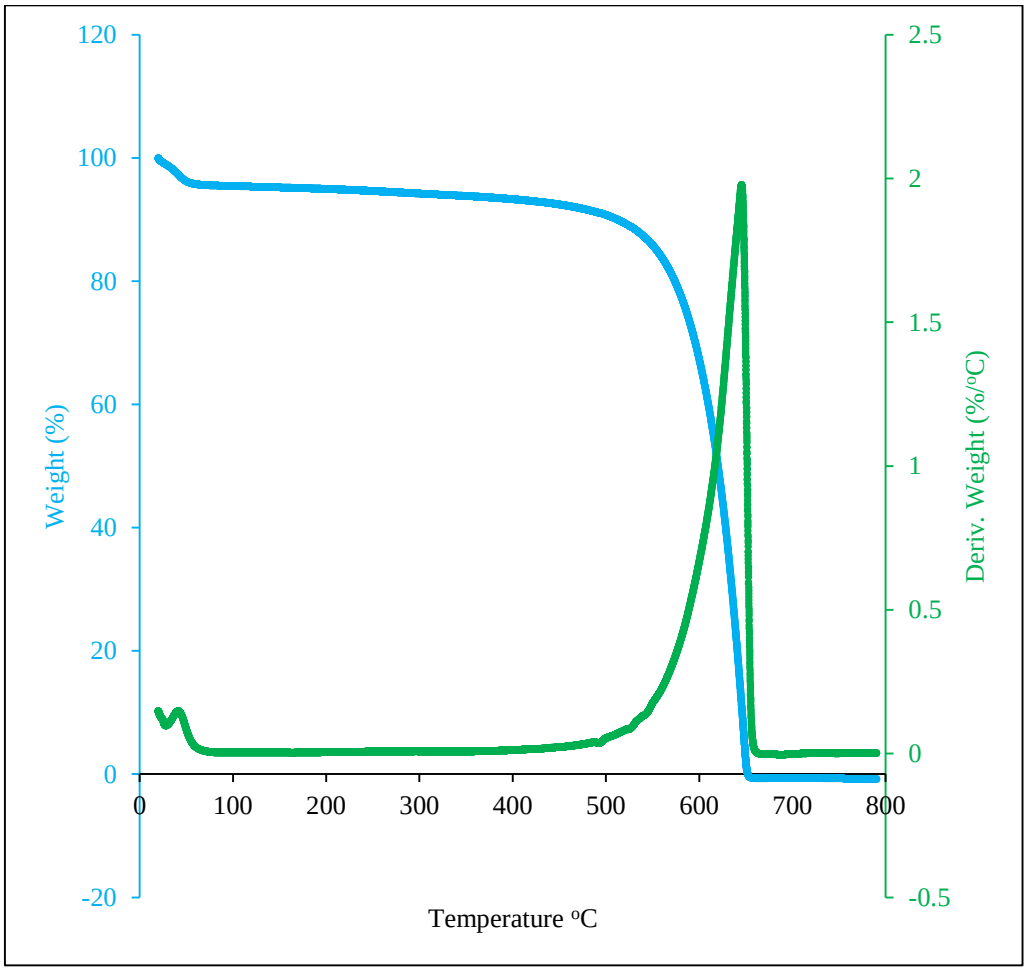


Figure 4.2: Thermo-gravimetric analysis result for acid treated fly ash from 7.106 mg, in alumina pan, temperature ramp 10°C/min to 800°C and air as flow gas with a flow rate of 100 mL/min.

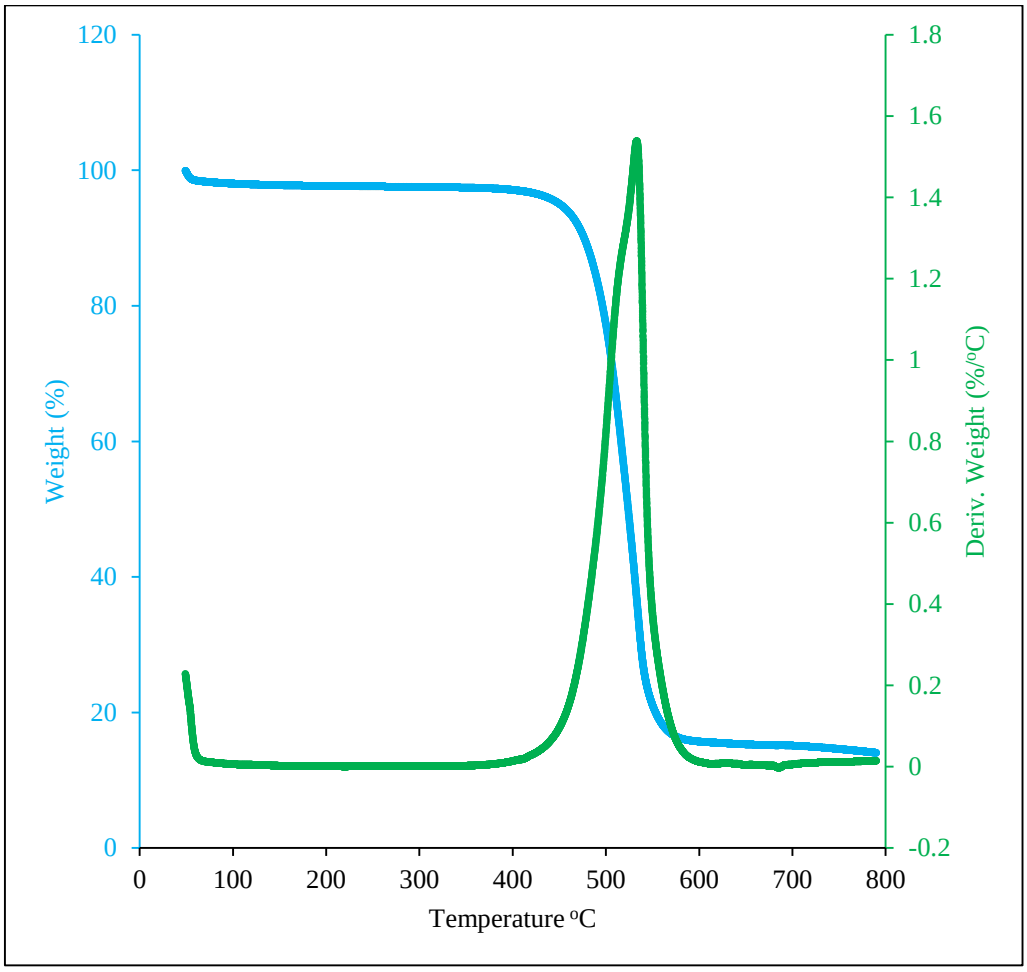


Figure 4.3: Thermo-gravimetric analysis result for ferric oxide impregnated fly ash from 7.890 mg, in alumina pan, temperature ramp 10°C/min to 800°C and air as flow gas with a flow rate of 100 mL/min.

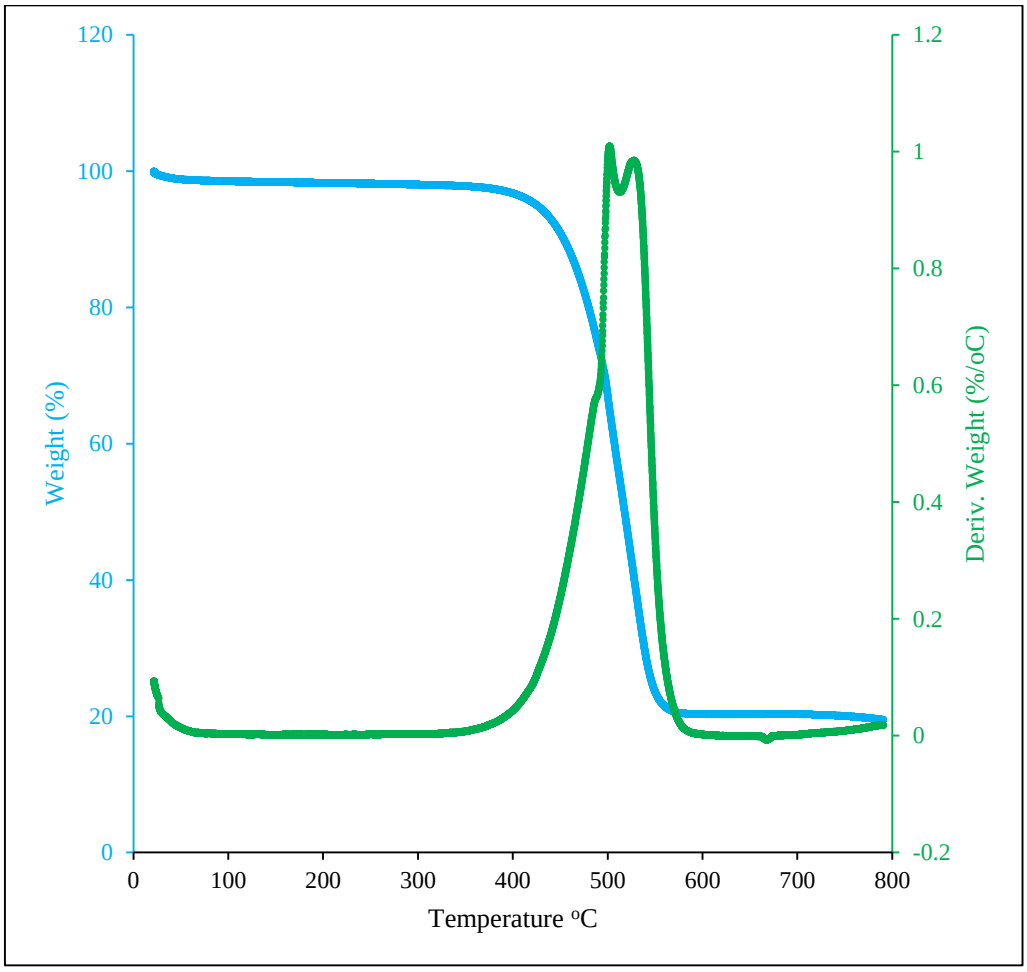


Figure 4.4: Thermo-gravimetric analysis result for silver oxide impregnated fly ash from 7.627 mg, in alumina pan, temperature ramp 10°C/min to 800°C and air as flow gas with a flow rate of 100 mL/min.

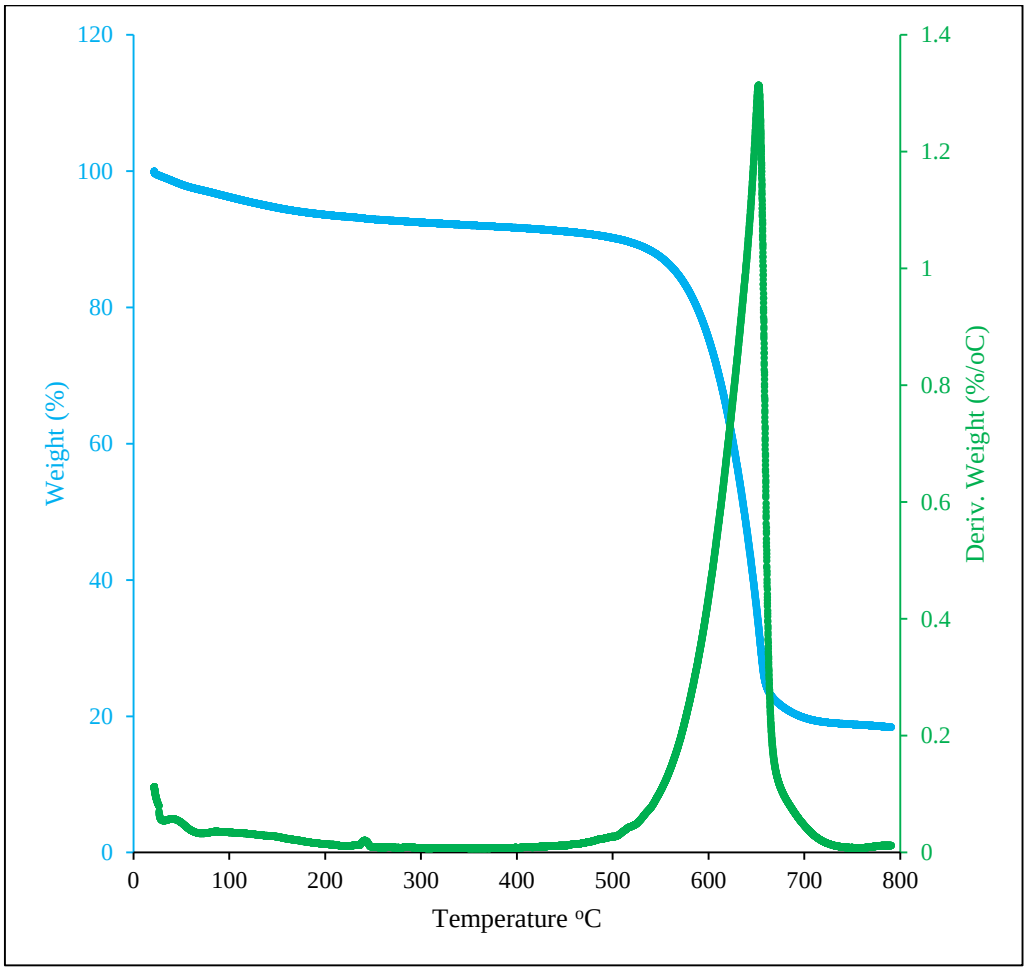


Figure 4.5: Thermo-gravimetric analysis result for aluminum oxide impregnated fly ash from 7.480 mg, in alumina pan, temperature ramp 10°C/min to 800°C and air as flow gas with a flow rate of 100 mL/min.

4.1.3 Field Emission Scanning Electron Microscopy (FESEM)

The FE-SEM micrograph (magnification x500) of the raw fly ash material (Figure 4.6), shows the orbicular and heterogeneous pore structure of the fly ash powder, having approximately 100 μm average grain diameter, with pores of different sizes on its surface. Figures 4.7 to 4.9 show various distribution of the metal nanomaterial on the surface of the fly ash, following impregnation and binding of the metal oxides to the pore spaces on the fly ash material. Surface area and pore volume distribution change are important physical observations following metal oxide impregnation of the fly ash. Other magnifications of the FE-SEM micrographs are collected in Appendix B.

4.1.4 Energy Dispersive X-Ray (EDX)

The micro-chemical analysis of raw fly ash material used in the study by EDX spectroscopy showed that it is mainly composed of carbon, with considerable amount of oxygen as shown in the EDX spectrum in Figure 4.10. The spectrum for the raw fly ash showed the existence of metal impurities, and Figure 4.11 shows that these metal impurities were significantly removed following treatment of the raw fly ash with nitric acid. This was important to prevent any form of cross-contamination of the aqueous solution from metal impurities attached to the fly ash during the liquid fuel combustion process. Also, from Figures 4.10 to 4.14, the micro-chemical analysis of metal oxide impregnated-fly ash showed the respective metals deposited on the surface of the fly ash to be in considerable amount. This served as an indication that the observed nanoparticles on the surface of the fly ash originated from the respective metal oxide impregnation.

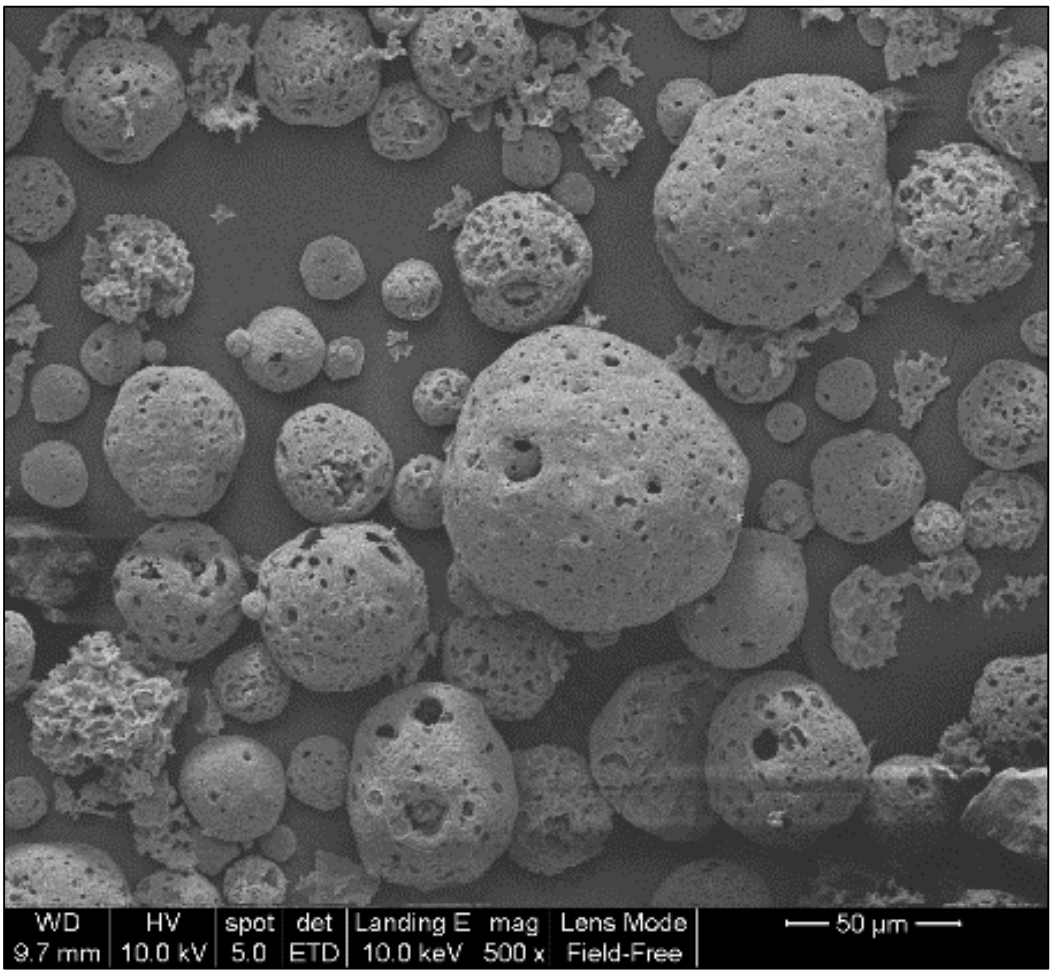


Figure 4.6: SEM micrograph of raw fly ash (magnification x500)

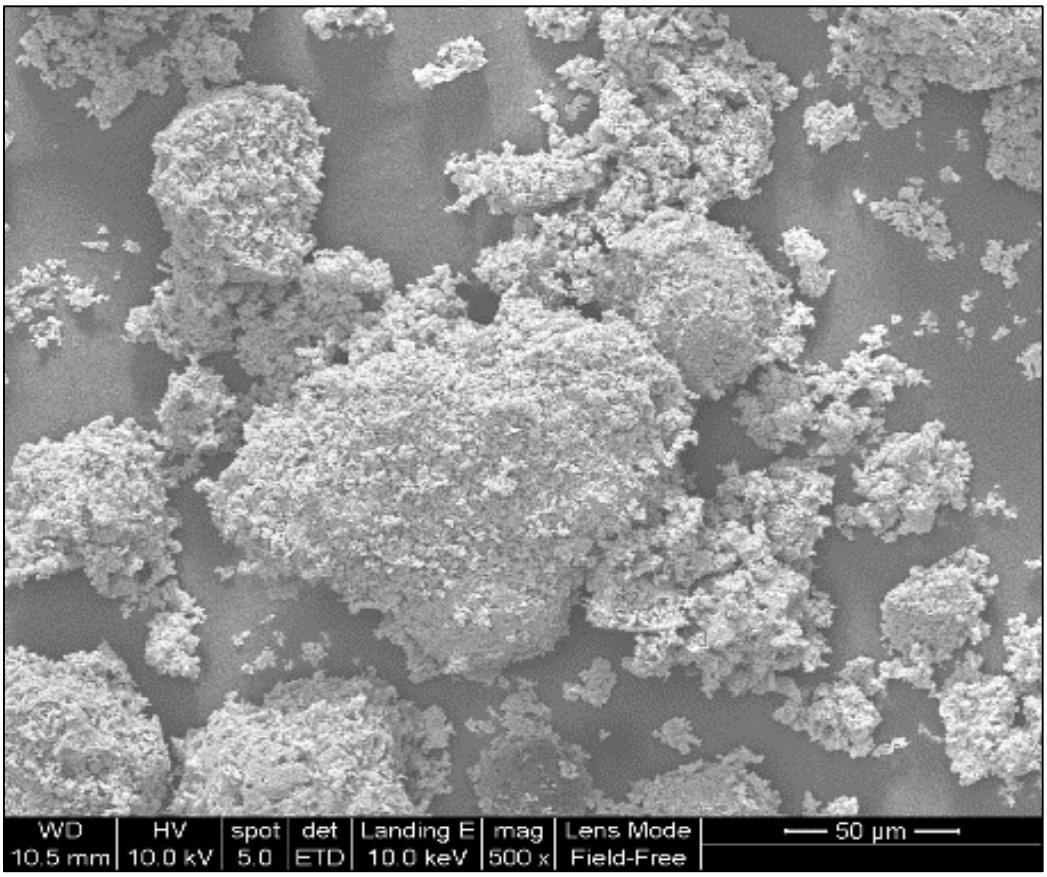


Figure 4.7: SEM micrograph of silver oxide impregnated fly ash (magnification x500)

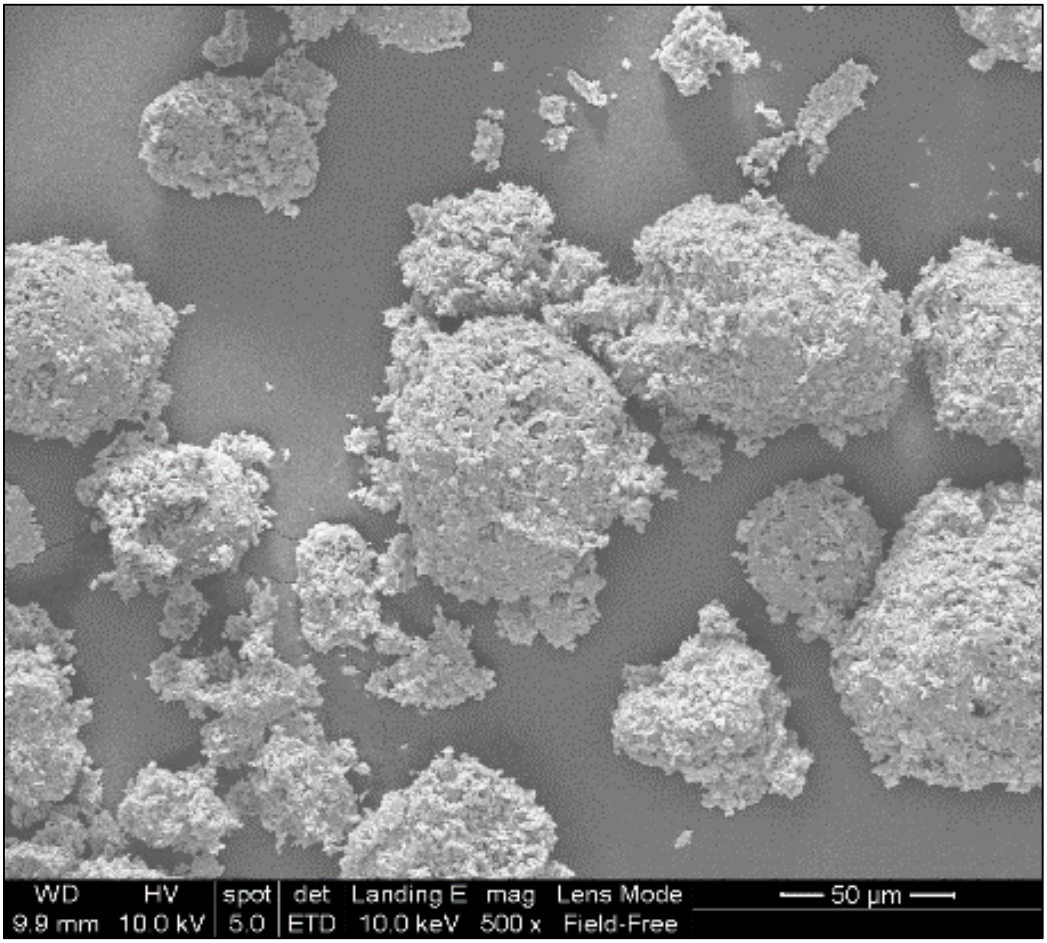


Figure 4.8: SEM micrograph of ferric oxide impregnated fly ash (magnification x500)

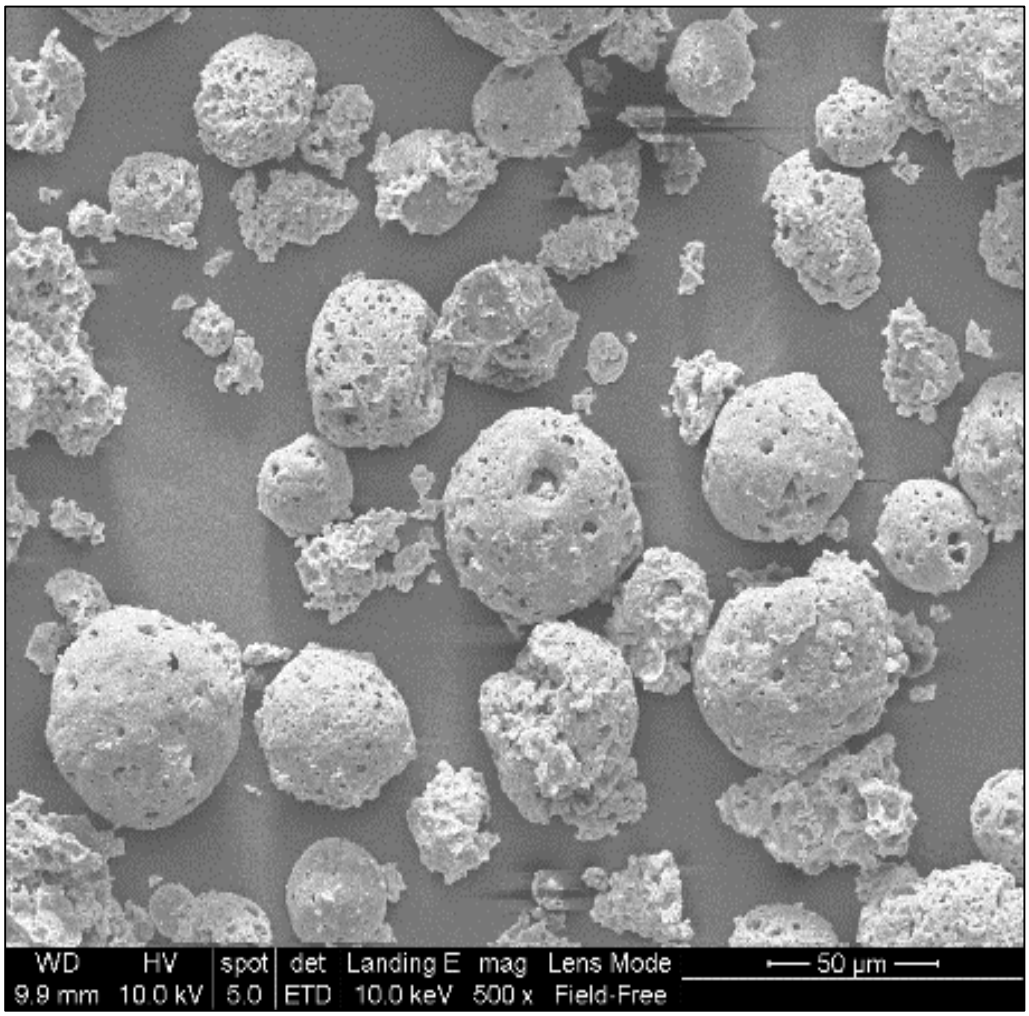


Figure 4.9: SEM micrograph of aluminium oxide impregnated fly ash (magnification x500)

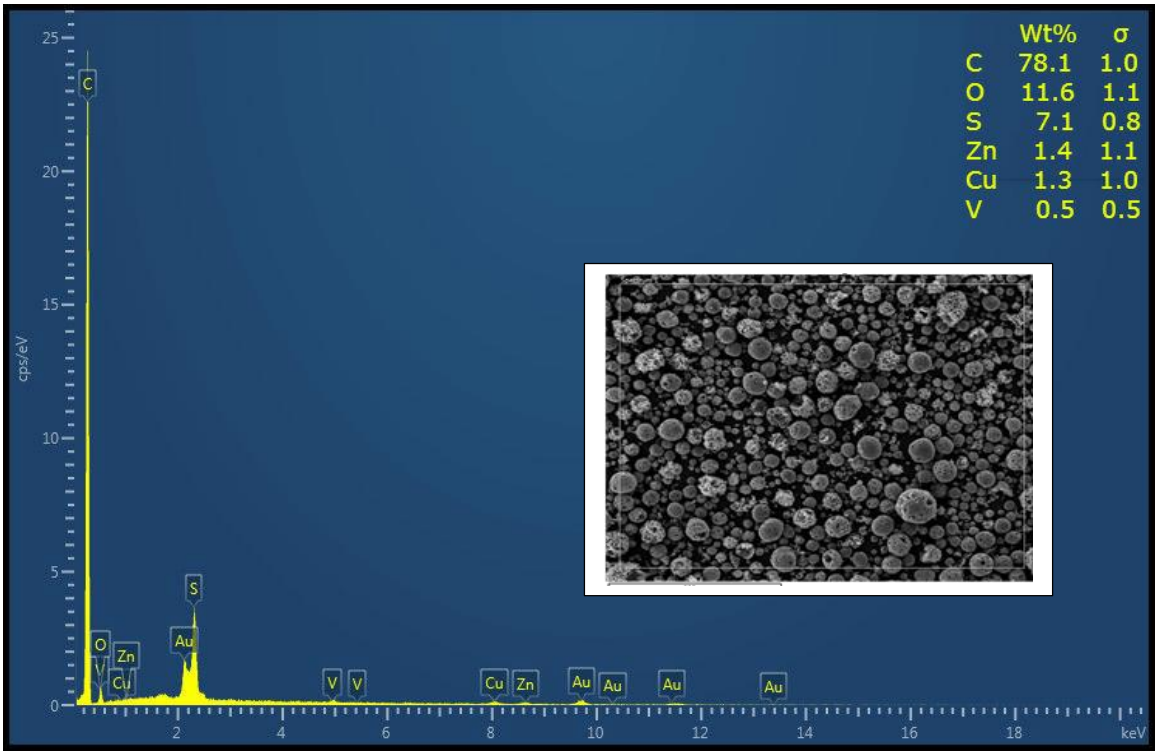


Figure 4.10: EDX spectrum of raw fly ash composite

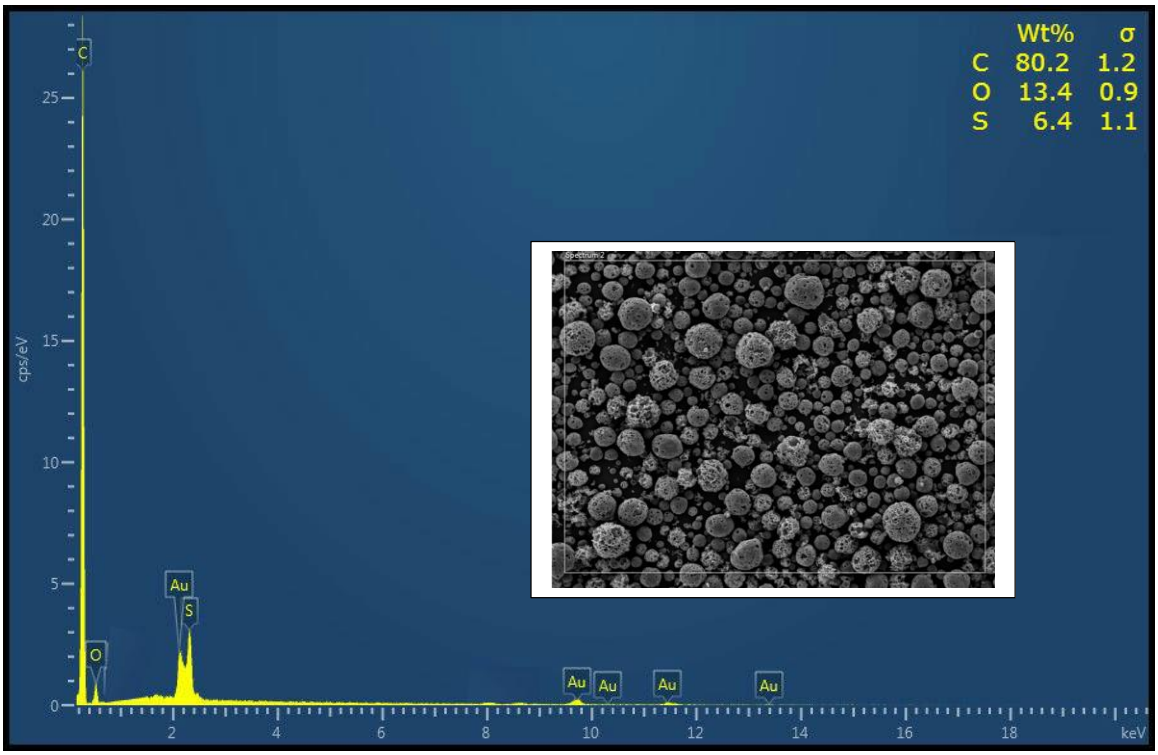


Figure 4.11: EDX spectrum of acid treated fly ash

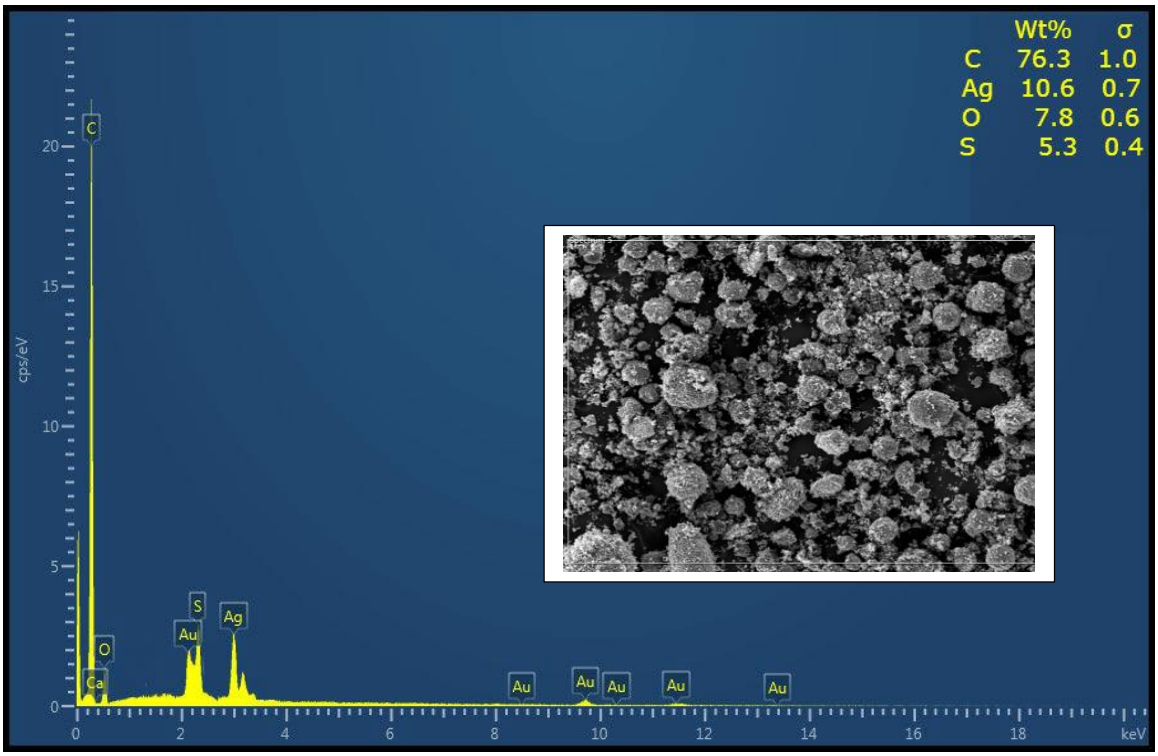


Figure 4.12: EDX Spectrum of silver oxide impregnated fly ash

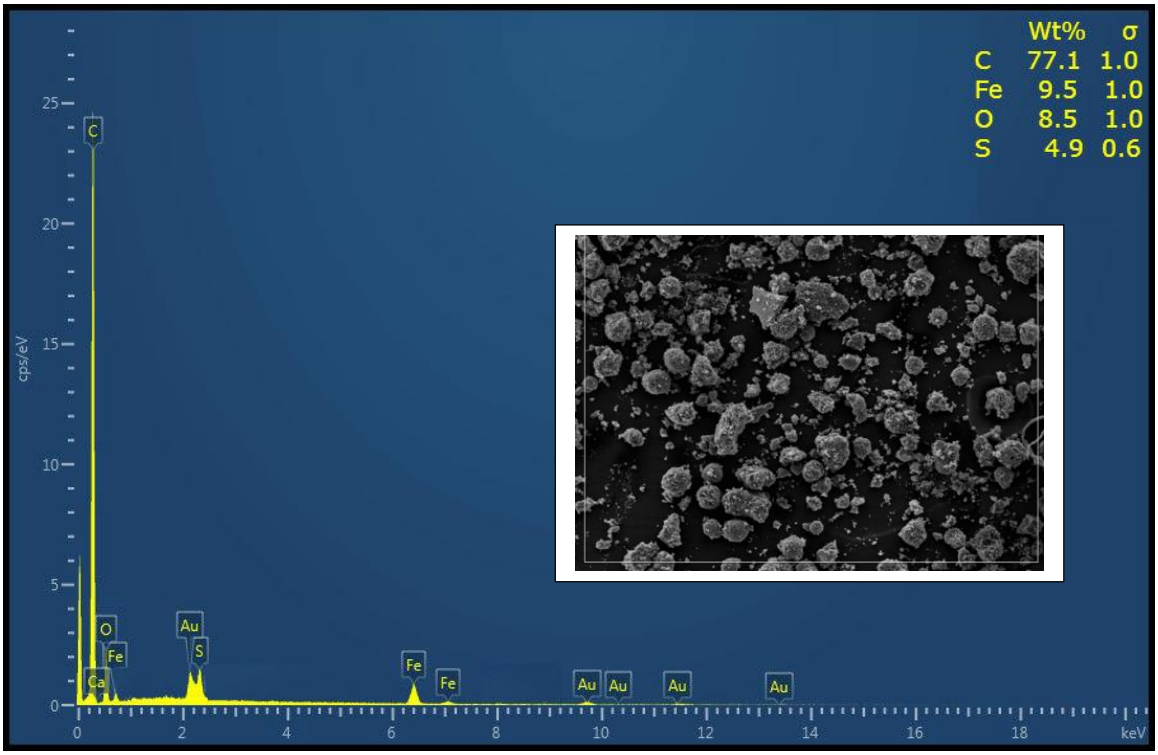


Figure 4.13: EDX Spectrum of ferric oxide impregnated fly ash

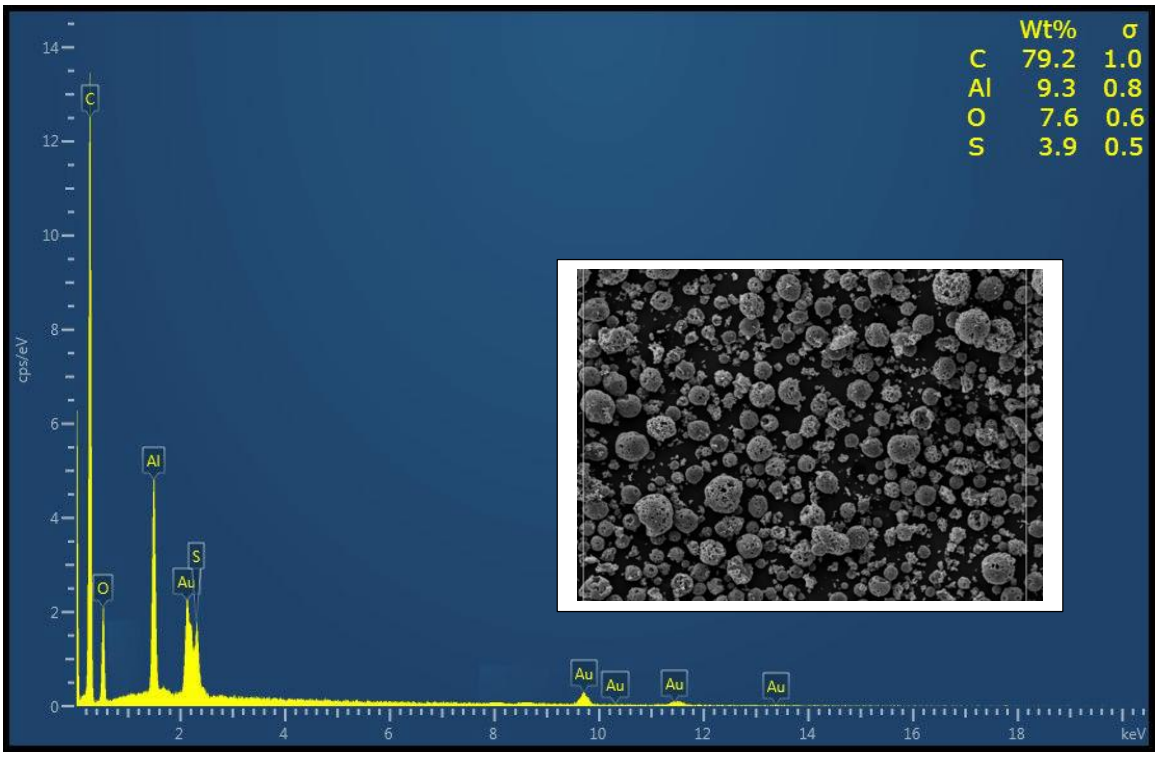


Figure 4.14: EDX Spectrum of aluminium oxide impregnated fly ash

4.2 Blank Batch Experiment Runs

In order to ensure that the recorded removal of MTBE from the aqueous solution is attributable to the adsorbent used, blank runs were conducted in which aqueous solution spiked with MTBE was agitated without any adsorbent added. The results from the blanks represented the loss of MTBE to the container and environment by volatilization. Based on this observation, the results of MTBE removal efficiencies reported in this work were obtained by deduction of the MTBE loss to the environment as obtained from the blank runs. Figure 4.15 shows a typical blank experiment result obtained during this study. The initial drop in the % reduction of MTBE can be attributed to the time during which MTBE becomes completely dissolved in the solution. Beyond this point, it was observed that loss of MTBE to the environment increased as the duration of the batch experiment extended, with a maximum of 10% loss to the environment.

4.3 Testing of Adsorbents for MTBE Removal

To understand the role of adsorbent type on the MTBE removal efficiency, screening of the different adsorbents prepared during this study was conducted to ascertain the adsorbent with highest potential for MTBE removal from the aqueous solution. Figure 4.16 shows that silver oxide impregnated fly ash (Ag_2O-FA) was the only tested adsorbent that brought about notable removal of MTBE from the aqueous solution. Other tested adsorbents did not show any significant removal of MTBE from the solution. This was attributed to the significant increase in surface area recorded for Ag_2O-FA relative to the other adsorbents. Additional study was conducted to obtain the optimum set of experimental conditions for Ag_2O-FA removal of MTBE from the spiked solution.

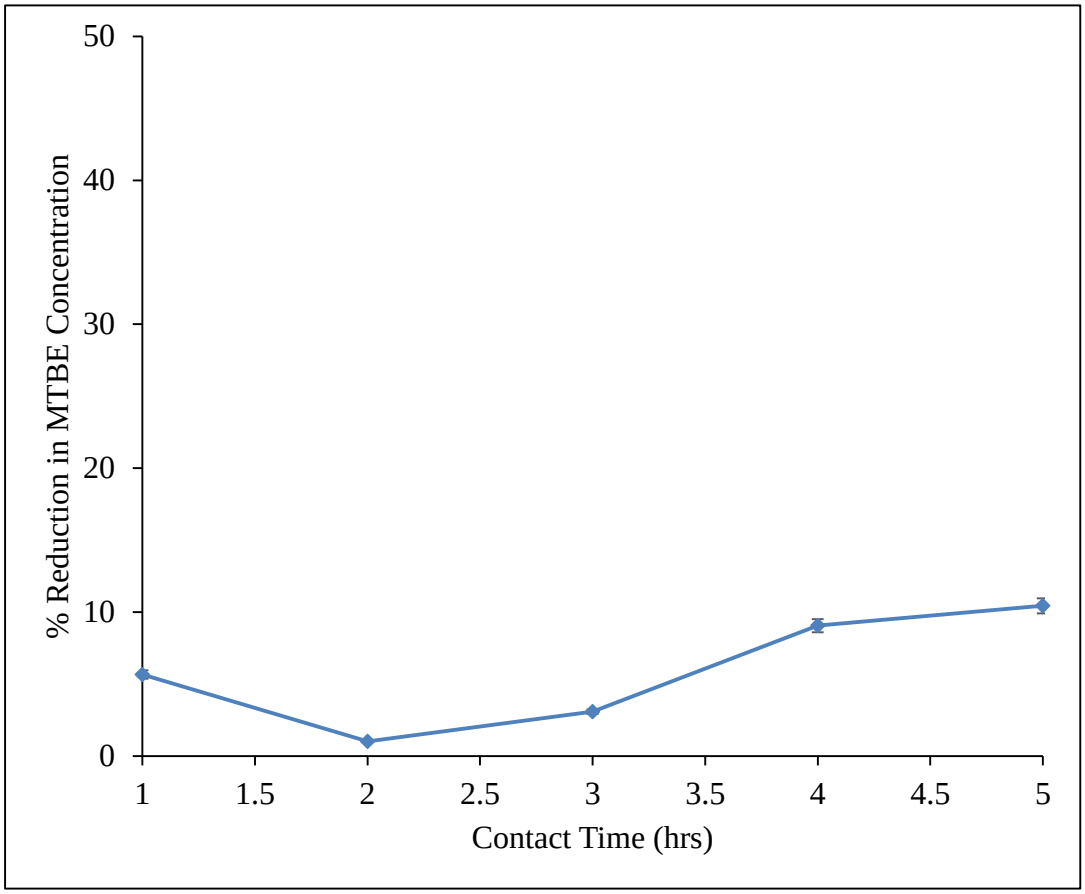


Figure 4.15: Blank batch experiments – % reduction in MTBE concentration in aqueous solutions without adsorbents at room temperature, 200rpm agitation speed and 1000 µg/L initial MTBE concentration

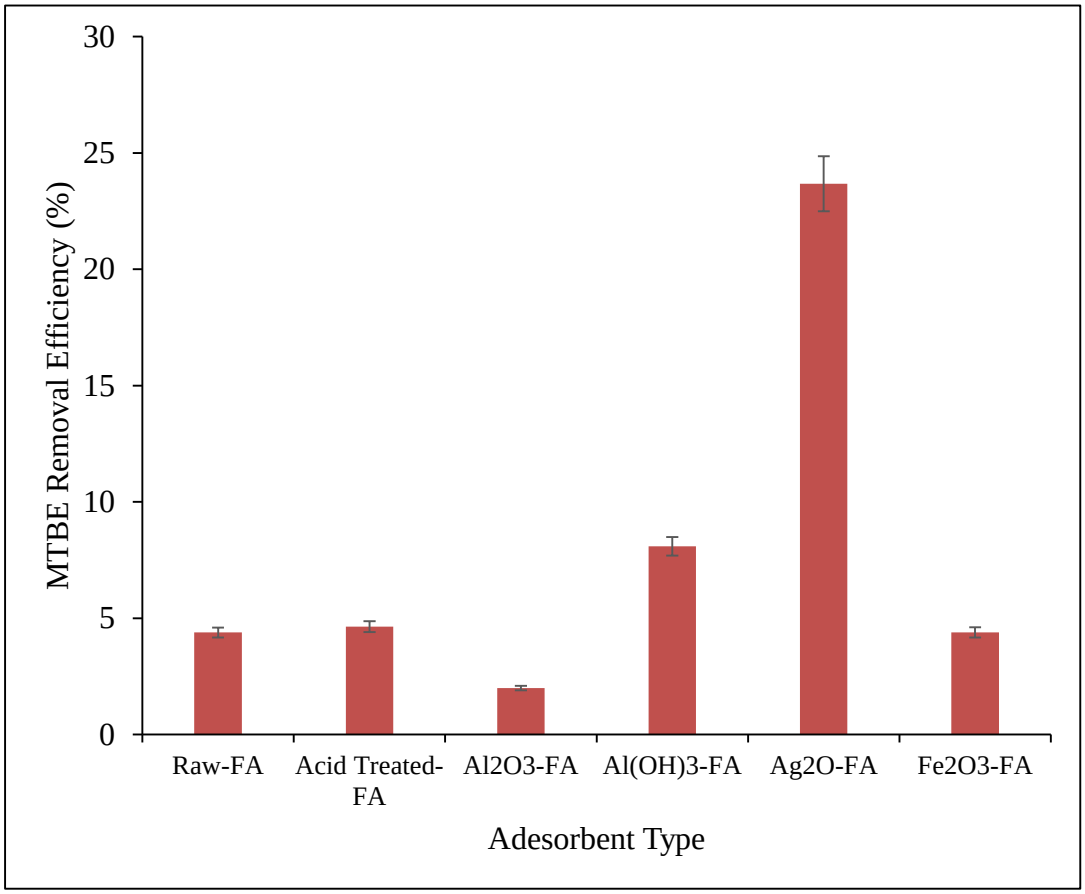


Figure 4.16: Role of adsorbent type on MTBE removal efficiency from aqueous solution at room temperature, pH 6, 50 mg adsorbent dosage, 2 hours contact time, 200rpm and 1000 µg/L initial MTBE concentration

4.4 Effects of Treatment Parameters on MTBE Removal

Following the establishment of silver oxide impregnated fly ash as the most efficient of the adsorbents prepared, various treatment parameters such as pH, agitation speed, contact time, and initial adsorbate concentration were assessed for their potential to improve the MTBE removal efficiency of the Ag_2O-FA.

4.4.1 Effect of pH on MTBE Adsorption by Fly Ash

The adsorption of MTBE by fly ash based adsorbent, with specific focus Ag_2O-FA at various pH values (3-9) for MTBE initial concentration of 1000 µg/L was assessed to determine the optimum removal pH. Although a significant time of this study was devoted to study the removal of MTBE at the pH of groundwater (6 ± 0.5), which is the potential matrix susceptible to MTBE contamination. From Figure 4.17, there was notable variation in MTBE adsorption behavior under different pH conditions for the non-modified fly ash and modified fly ash. For the non-modified fly ash, there was no significant change in the removal efficiency across the pH range (3 – 9) that was studied. However, for the modified fly ash, the removal efficiency increased with decrease in the pH of solution, with pH 3 being the highest. This observation was attributed to decrease in MTBE solubility at lower pH condition, thereby enhancing adsorption. Ghadiri *et al.*, (2010) reported similar increase in MTBE removal efficiency with decrease in solution pH using hexadecyltrimethylammonium chloride (HDTMA) modified zeolite as adsorbent. For both adsorbent materials, 100 mL of MTBE spiked deionized water, agitation speed of 200rpm, contact time of 2 hours, 75 mg dosage of material and initial MTBE concentration of 1000 µg/L were used in the pH study.

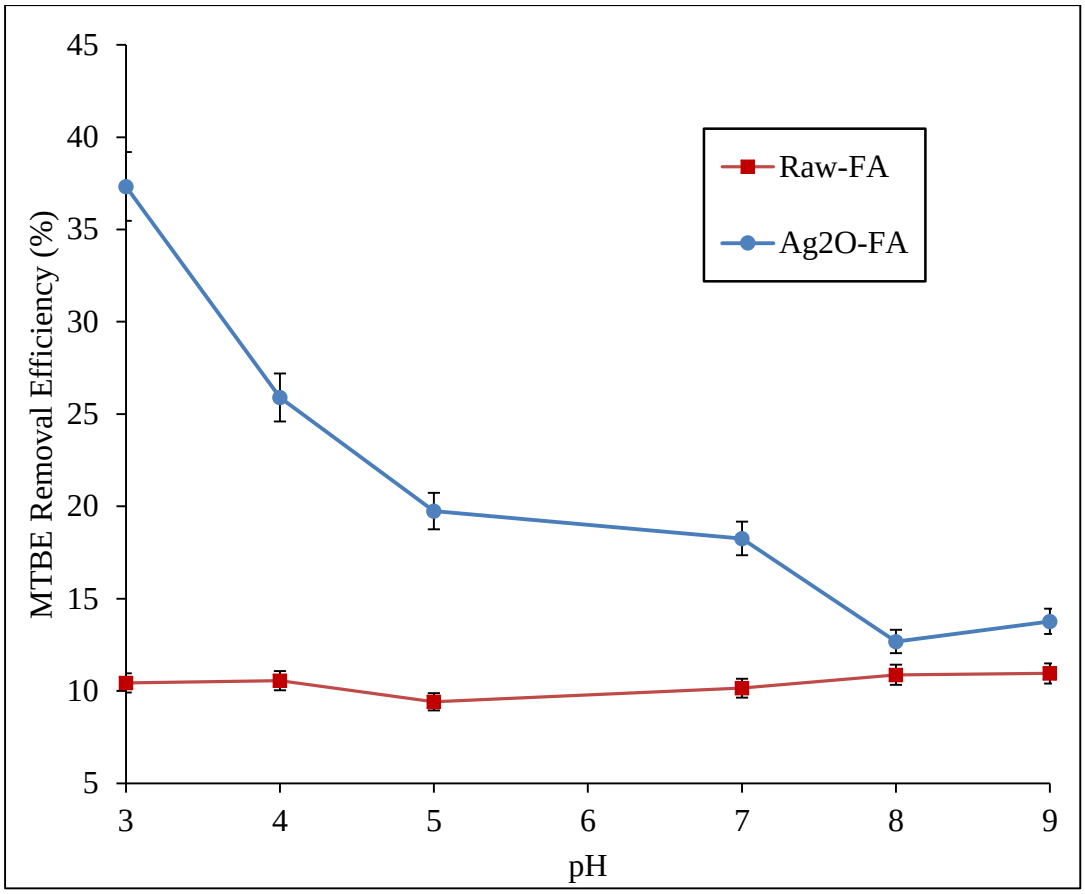


Figure 4.17: Effect of pH on MTBE adsorption behaviour of non-modified (raw fly ash) and modified fly ash (silver oxide impregnated) at room temperature, 200rpm agitation speed, 75 mg adsorbent dosage, 2 hours contact time and 1000 µg/L initial MTBE concentration

4.4.2 Effect of Agitation Speed on MTBE Adsorption

Adsorption, being the mechanism of treatment used in this study, required contact between the surface of the adsorbent material and the target adsorbate (MTBE). During the course of the batch experiments, it was observed that at agitation speed of 150rpm, the adsorbent materials were settled at the base of the conical flask, having limited contact with the solution and a potential negative impact on the expected removal. At agitation speed of 200rpm, more contact was observed between the adsorbent material and the solution. The speed was however not increased beyond 200rpm in order to minimize loss of MTBE by volatilization during the agitation process. A comparison of the percentage removal of MTBE from the aqueous solution using raw-FA and Ag_2O-FA with agitation speeds from 50 to 200rpm was conducted and result summarized in Figure 4.18. The observed increase in removal efficiency with increase in agitation speed was attributed to improved contact between the active adsorption sites on the adsorbent materials and MTBE in the solution, which enhanced formation of the needed van der Waals forces for physical adsorption.

4.4.3 Effect of Adsorbent Dosage on MTBE Adsorption

In order to understand the role of adsorbent dosage on the adsorption of MTBE, six (6) different adsorbent materials (raw fly ash, acid treated fly ash, aluminum oxide impregnated fly ash, aluminum hydroxide coated fly ash, silver oxide impregnated fly ash and ferric oxide impregnated fly ash) were prepared and tested for their adsorption capacity. In this study, the agitation speed was fixed at 200rpm, initial MTBE concentration of 1000 µg/L, pH 6 and contact time of 2 hours.

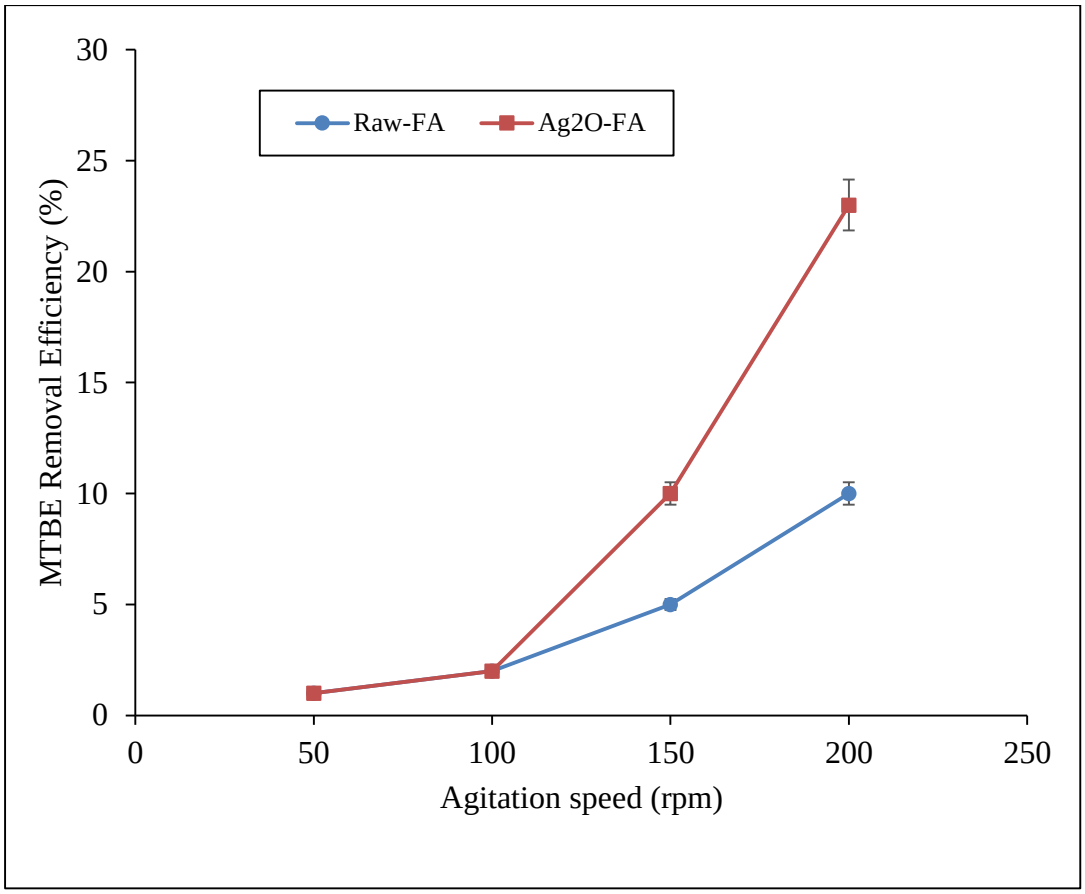


Figure 4.18: Effect of agitation speed on MTBE adsorption behavior of non-modified fly ash (raw fly ash) and modified fly ash (silver oxide impregnated) at room temperature, pH 6, 75 mg adsorbent dosage and 1000 µg/L initial MTBE concentration

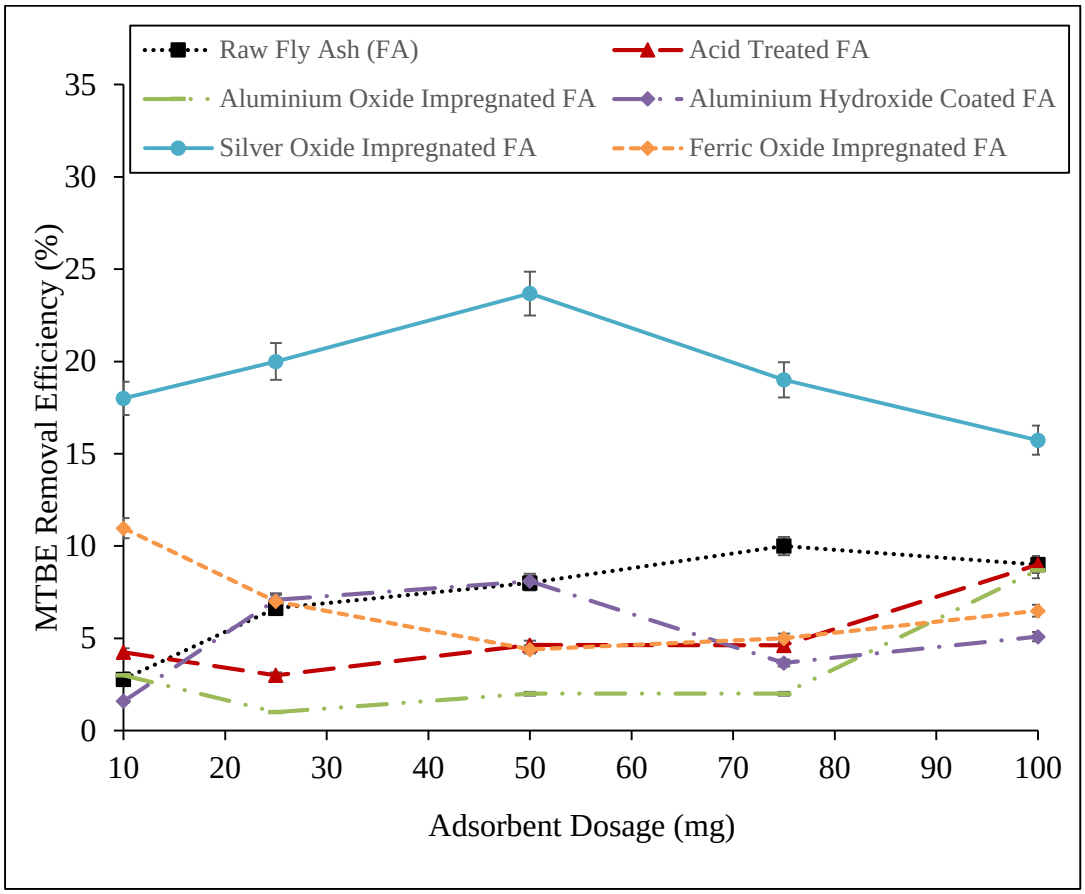


Figure 4.19: Effect of adsorbent dosages (mg) on MTBE adsorption behavior of different adsorbent materials at room temperature, 200rpm agitation speed, pH 6, 2 hours contact time, and 1000 µg/L initial MTBE concentration

From Figure 4.19, it would be noted that with the exception of silver oxide impregnated fly ash, there was no significant variation in the adsorption capacity of all other adsorbent material with change in dosage. However, with silver oxide impregnated fly ash, an increase in removal efficiency was noted with increase in dosage of adsorbent material until the optimum dosage was reached, beyond which a decrease in adsorption was observed with increase in adsorbent material. A peak reduction of 24% was noted at 50 mg of adsorbent and further increase in adsorbent resulted in decline in adsorption. The availability of more adsorption sites due to increase in adsorption surface can be assumed responsible for the increase in MTBE adsorption with increase in adsorbent dosage (Senthilkumar *et al.,* 2010). The decline in adsorption with further increase in dosage beyond 50 mg can be attributed to overlapping or aggregation of adsorption sites resulting in reduction in the surface area available for MTBE adsorption, with El-Sayed (2011) reporting similar behavior in an adsorption study of methylene blue.

4.4.4 Effect of Contact Time on MTBE Adsorption

The contact time is another variable which is expected to have an important role in the adsorption process. The contact time required to reach optimum adsorption varies generally, depending on the nature of interaction occurring between the adsorbent and adsorbate. In this study, the interaction was observed to be physical adsorption and this effect was assessed for all the prepared adsorbent materials during the batch experiments. Different dosages (10 – 100 mg) of the adsorbent materials were also used in this test to evaluate whether the behavioral pattern will differ with dosage alteration. From Figure 4.20, it was observed that the dosage of the adsorbent did not affect their adsorption behavior with time, as similar trends were observed for the different dosages of the

adsorbent materials tested. The adsorption of MTBE by fly ash (irrespective of form) was found to increase with time till 2 hours of contact with the adsorbent, after which there was a slight and gradual decline in the adsorption. This observation can be explained by the adsorption equilibrium phenomenon, in which the rate of adsorption was greater than the rate of desorption until equilibrium was reached at the contact time of 2 hours, in which the adsorption sites on the adsorbent were saturated. Beyond this point, the rate of desorption was greater than the rate of adsorption, accounting for the slight and gradual decline in the MTBE adsorption beyond the optimum time of 2 hours. Li *et al.,* (2012) also reported 10% desorption upon use of modified oil sludge (MOS) for MTBE removal from aqueous solution.

4.4.5 Effect of Initial MTBE Concentration on Adsorption

Depending on the type of interaction occurring between the adsorbent and adsorbate, there is generally a decrease in the percentage removal with increase in concentration of the adsorbate. The decline is usually attributed to the saturation of the adsorption sites on the adsorbent material, hence a decrease in the surface area available for adsorption as the active sites on the adsorbent surface are occupied (Salleh *et al.,* 2011; Kannan and Sundaram, 2001). In this study, there was however a deviation from the above general observation, which may be attributed to the unique properties of MTBE in water. The high solubility of MTBE in water (50,000 mg/L) and its low organic-carbon partition coefficient KOC (11 mg/L) make adsorption a challenging technique for its removal from aqueous media.

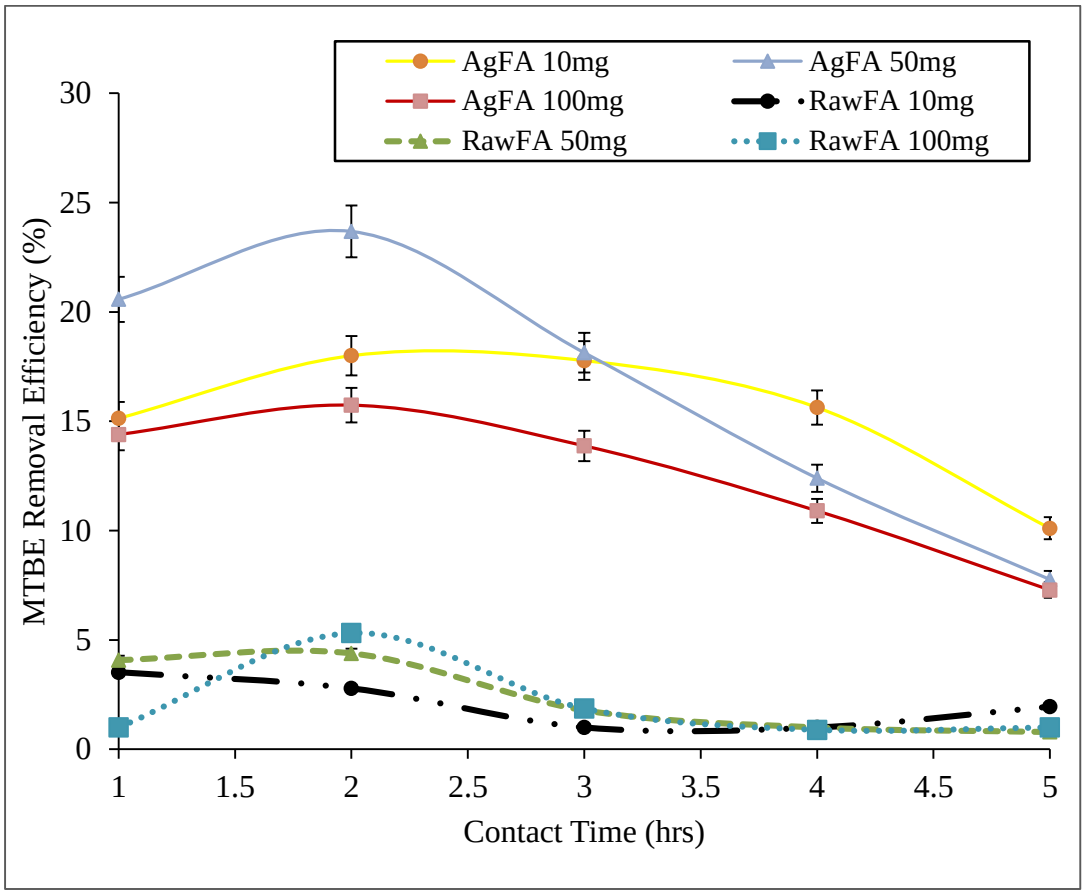


Figure 4.20: Effect of contact time on MTBE adsorption behaviour by raw fly ash and Ag_2O impregnated fly ash at room temperature, 200rpm agitation speed, pH 6 and 1000 µg/L initial MTBE concentration

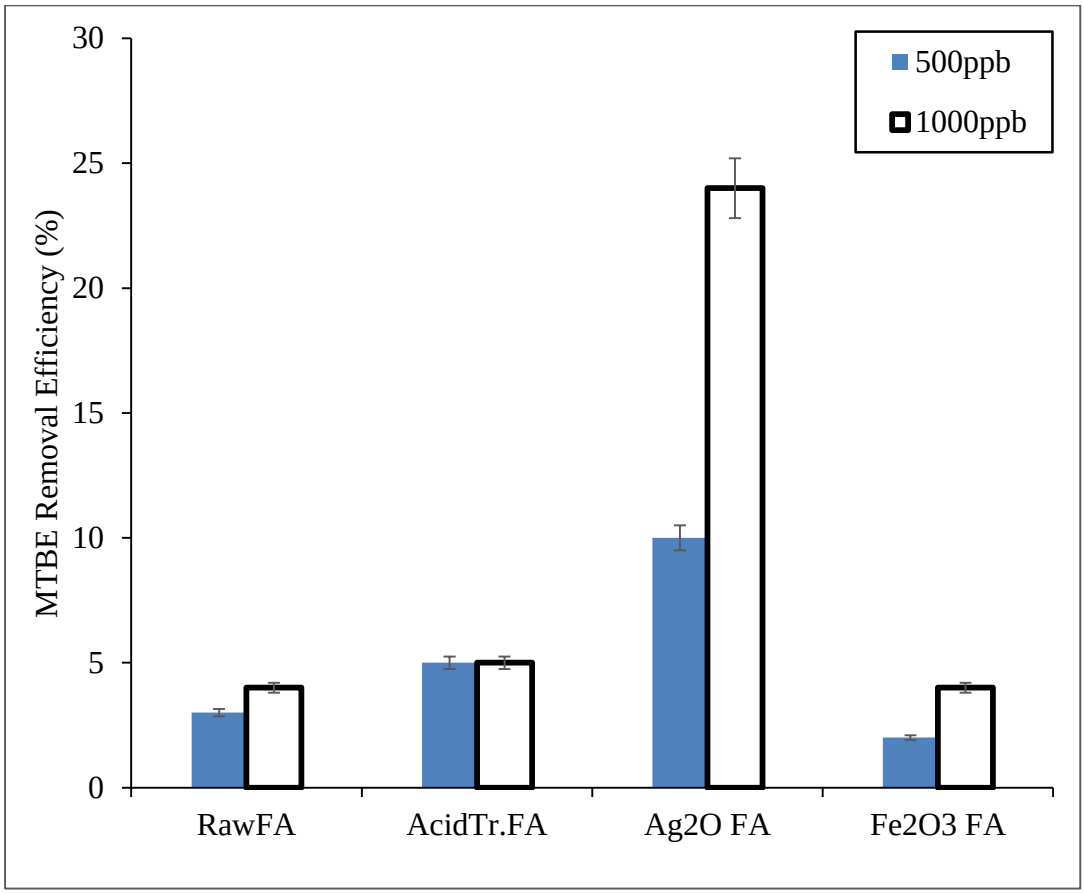


Figure 4.21: Effect of initial MTBE concentration on adsorption behavior at room temperature, 50 mg adsorbent dosage, 200rpm agitation speed, pH 6 and 2 hours contact time

From Figure 4.21, with the silver oxide impregnated fly ash, there was a notable increase from 10% to 24% in the removal efficiency with an increase in the initial MTBE concentration from 500 µg/L to 1000 µg/L. This observation was attributed to the distribution of MTBE in the solution, at low concentration, high distribution of the molecules in the solution did not favor adsorption. However, a denser solution at the higher concentration favored adsorption, as more bombardment and contact occurred between the MTBE molecules and the active adsorption sites on the silver oxide impregnated fly ash.

4.5 Comparison with Adsorption of MTBE by Activated Carbon

In order to better understand the mechanism of removal of MTBE from the aqueous solution using adsorbent materials, activated carbon was subjected to same experimental conditions as with the fly ash materials used in this study.

4.5.1 Removal of MTBE using Activated Carbon alone

In order to establish a baseline for comparison of subsequent combination of variables, the efficiency of activated carbon (AC) alone for the removal of MTBE in aqueous solution was studied. From Figure 4.22, it was observed that there was an increase in the MTBE removal efficiency of AC with increase in dosage. Similar to the observation made from the use of silver oxide impregnated fly ash (Ag_2O-FA), there was an increase in percentage removal with time and the optimum removal of 71% was achieved for 100 mg of activated carbon at 2 hours contact time, which was the equilibrium point, as there was no significant change in the percentage removal beyond this point.

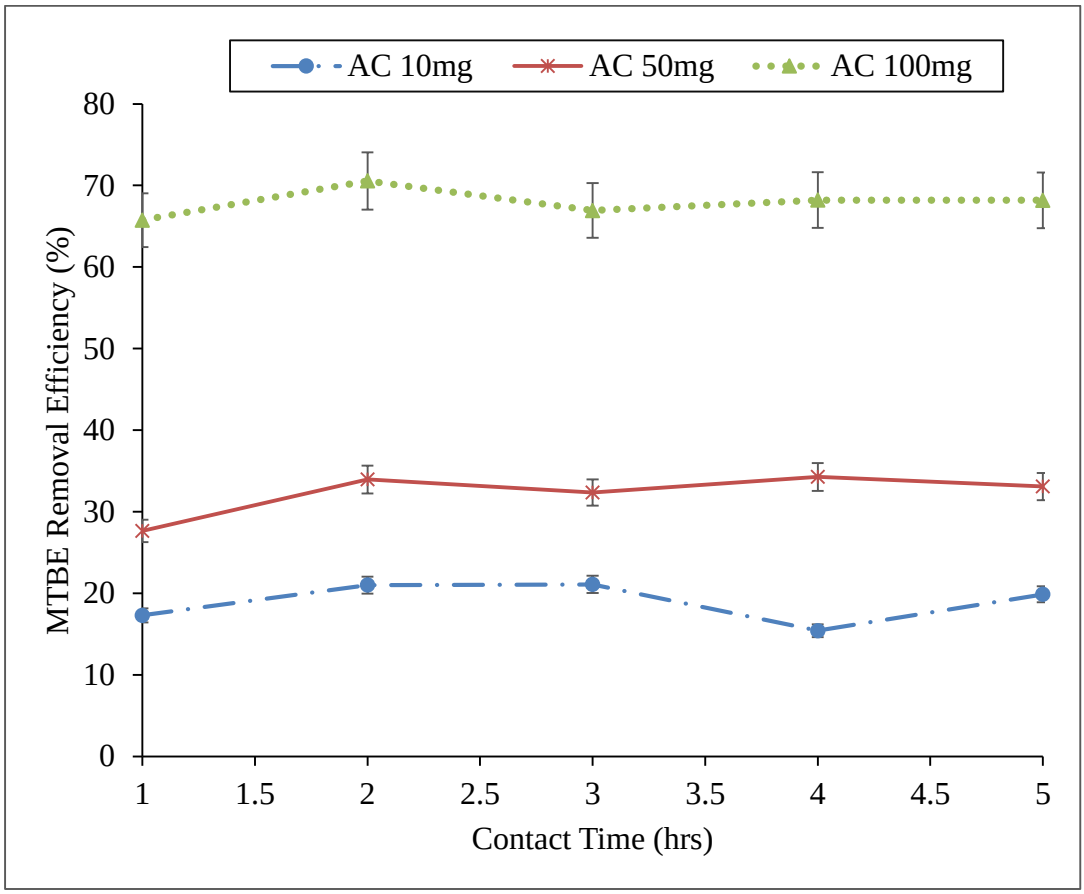


Figure 4.22: Percentage removal of MTBE in aqueous solution at various dosages of activated carbon at room temperature, 200rpm agitation speed, pH 6 and 1000 µg/L initial MTBE concentration

4.5.2 Removal of MTBE using Activated Carbon Combined with Raw Fly Ash

In order to understand the potential for synergistic removal of MTBE from aqueous solution, a mixture of the raw fly ash and activated carbon in ratio of 1:1 (by weight) was utilized. The result, which was compared to the benchmark already established from the application of activated carbon alone. From Figure 4.23, it was noted that the raw fly ash had no notable contribution to the adsorption of MTBE from the aqueous solution, as there was no significant difference in the optimum percentage removal for 50 mg of activated carbon and the 50 mg adsorbent mixture ratio 1:1 of AC and raw-FA.

4.5.3 Removal of MTBE using Activated Carbon Combined with Ferric Oxide Impregnated Fly Ash

Similar to the study on synergistic effect conducted using activated carbon and raw fly ash, a mixture of activated carbon and ferric oxide impregnated fly ash was studied. The objective was to ascertain whether combining the ferric oxide (Fe_2O_3-FA) impregnated fly ash with activated carbon will increase the overall removal of MTBE from the aqueous solution in the batch experiment. 50 mg mixing ratio 1:1 (by weight) was also utilized in this study, with all other parameters same as earlier, and the result was benchmarked against that obtained from activated carbon alone. From Figure 4.24, it was observed that the combination equally failed to yield MTBE removal efficiency as much as was achieved from the use of AC alone. This can be attributed to the extremely large surface area of AC as compared to the fly ash used in this study. Although ferric oxide impregnation improved the surface area, it was unable to compete with that of the established activated carbon.

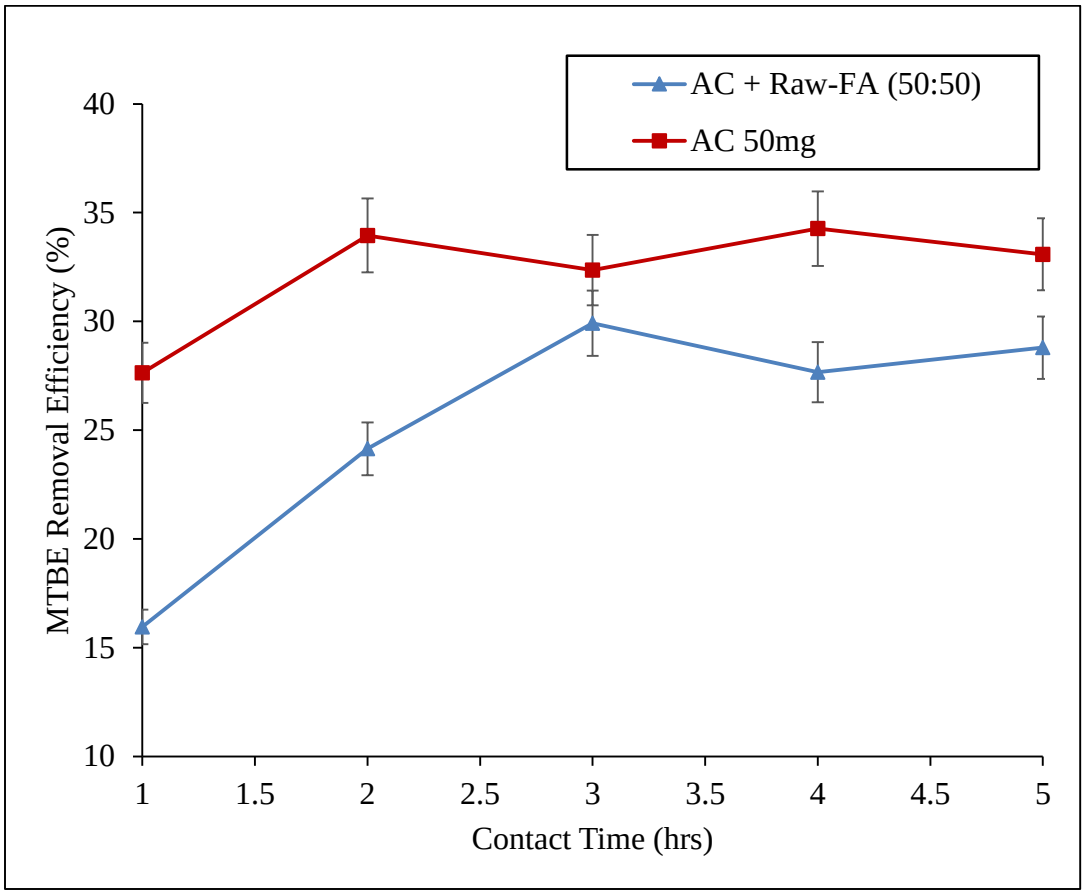


Figure 4.23: Percentage reduction in MTBE concentration for activated carbon alone compared with AC-raw fly ash mixture at room temperature, pH 6, 200rpm agitation speed and 1000 µg/L initial concentration

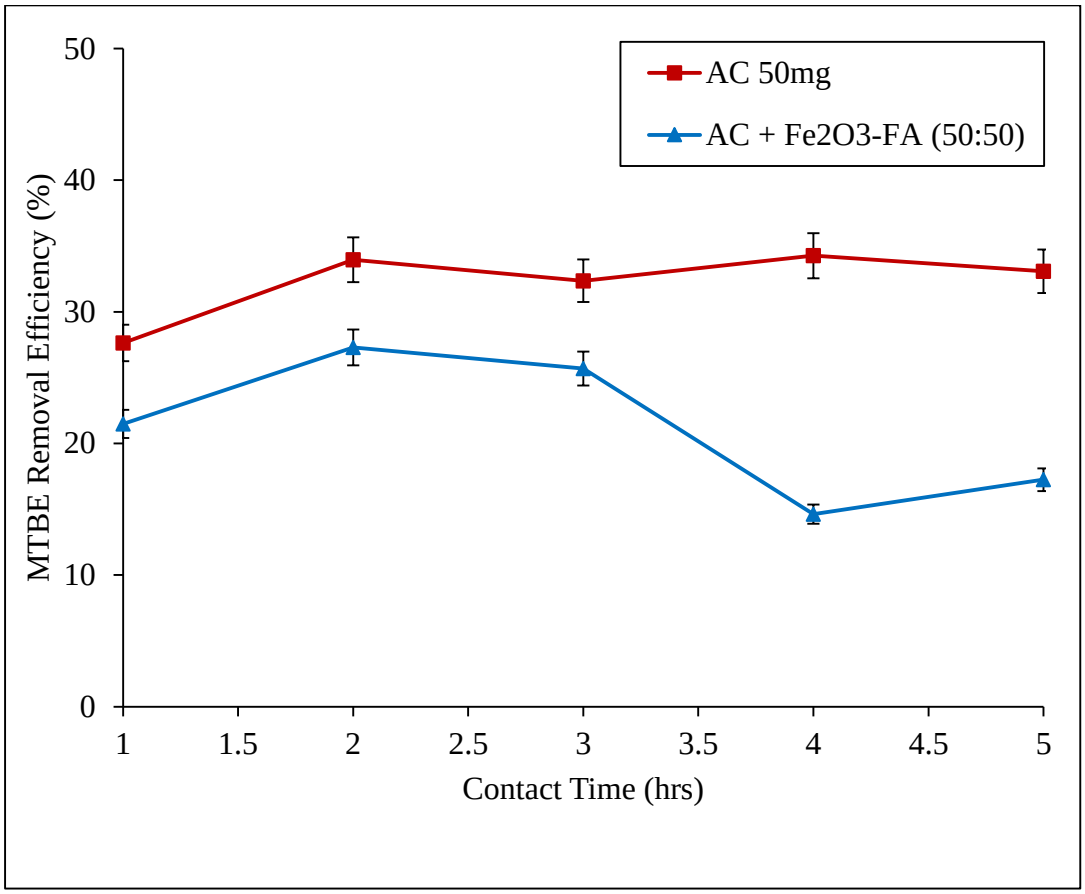


Figure 4.24: Percentage reduction in MTBE concentration for activated carbon alone compared with AC-ferric oxide impregnated fly ash mixture at room temperature, pH 6, 200rpm agitation speed and 1000 µg/L initial concentration

4.5.4 Removal of MTBE using Activated Carbon Combined with Silver Oxide Impregnated Fly Ash

Further study on the potential synergistic removal of MTBE was conducted in similar manner as was previously done, but with activated carbon and silver oxide impregnated fly ash mixture. Similar experimental conditions were adopted for this study, the mixture was in ratio 1:1 (by weight) and result was benchmarked against that from activated carbon alone. From the result shown in Figure 4.25, there was no significant difference in the results from activated carbon alone and the combination of activated carbon and silver oxide impregnated fly ash. This observation may be attributed to the higher surface area of the silver oxide impregnated fly ash as compared to the other fly ash based adsorbents. Also, the silver oxide impregnated fly ash did not interfere with adsorption behavior of the activated carbon, it rather contributed in adsorbing some of the MTBE in the solution, improving the overall adsorption.

4.5.5 Removal of MTBE using Silver Oxide Impregnated Activated Carbon

To better understand the role of silver oxide in the removal of MTBE using the impregnated fly ash, further study on its effect on the efficiency of activated carbon was conducted. In this study, activated carbon was impregnated with 10% silver oxide from silver nitrate in similar procedure as was done for fly ash and used in the batch treatment experiment. The results obtained shown in Figure 4.26, indicated a decline in the percentage reduction of MTBE with silver oxide impregnated activated carbon as compared to the use of activated carbon alone. For the 10 mg and 50 mg dosages of adsorbent materials, there was no significant difference in the MTBE removal

efficiencies upon impregnation with silver oxide, however better removal was achieved with AC alone than with Ag_2O-AC, as a drop from 71% to 53% was observed when 100 mg dosage of adsorbent was used. This observed decline may be attributed reduction in adsorption sites on the adsorbent's surface following impregnation with silver oxide. The BET surface area analysis further confirmed this, as there was a surface area decrease from 1,126.6314 m^2/g to 1,039.477 m^2/g for AC following silver oxide impregnation. This result prompted the conclusion that the removal process was mainly physical in nature and that for low surface area materials like fly ash, silver oxide impregnation resulted in surface area increase which improved its removal efficiency, however, for high surface area material such as AC, silver oxide impregnation resulted in decrease in its surface area, which brought about a drop in its adsorption capacity and MTBE removal efficiency.

4.6 Optimum Conditions for the Removal of MTBE

From the batch treatment experiments Ag_2O impregnated FA was observed to achieve the optimum removal of MTBE from aqueous solution, with peak removal efficiency of 24%. The solution's pH was also observed to influence the MTBE removal efficiency of silver oxide impregnated fly ash, with the peak removal achieved at pH 3. The optimum dosage was 50 mg and removal efficiency increased with increase in agitation speed, with 200rpm being the peak. Also, the adsorption equilibrium was attained after 2 hours of contact. The mechanism of MTBE removal in this study was by physical adsorption, as the absence of MTBE oxidation by-products eliminated the possibility of catalytic oxidation being responsible for the removal recorded under this study conditions.

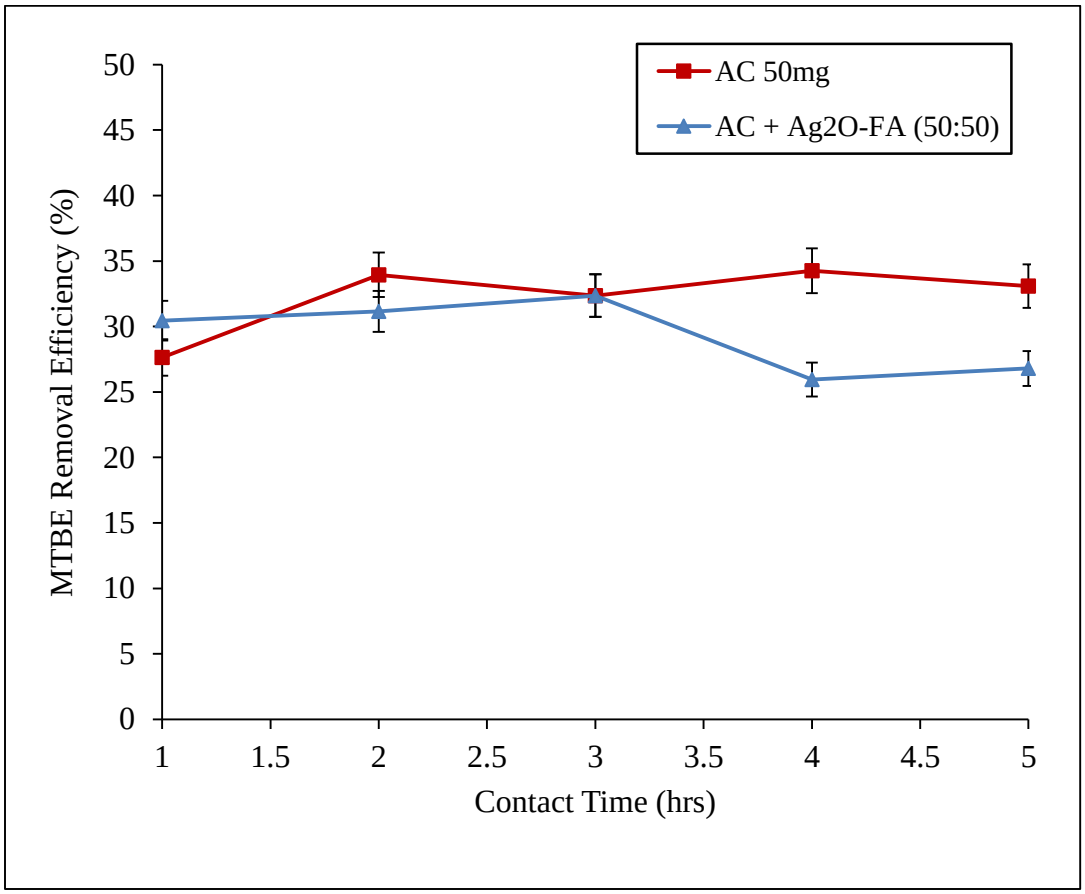


Figure 4.25: Percentage reduction in MTBE concentration for activated carbon alone compared with AC-silver oxide impregnated fly ash mixture at room temperature, pH 6, 200rpm agitation speed and 1000 µg/L initial concentration

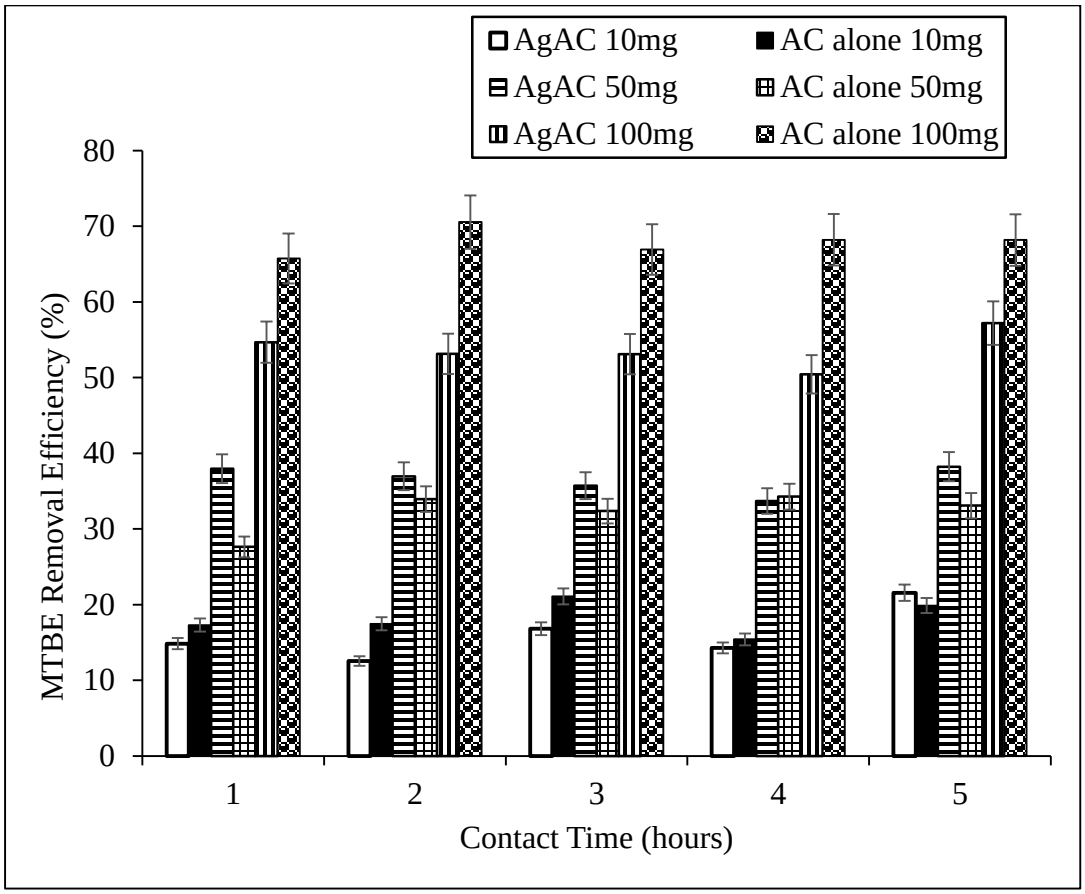


Figure 4.26: Percentage reduction in MTBE concentration for activated carbon alone compared with silver oxide impregnated activated carbon at room temperature, pH 6, 200rpm agitation speed and 1000 µg/L initial concentration

4.7 Adsorption Isotherms Study

Understanding the adsorption isotherms is crucial because important information on the surface properties, affinities and the adsorption mechanism of the adsorbent material are emphasized (Santhi *et al.,* 2010). Models important for the description of adsorption behavior are usually provided by the adsorption isotherm. The distribution of adsorbate molecule between the liquid phase and solid phase at the equilibrium state can be indicated by the adsorption isotherm. In this study, Langmuir and Freundlich isotherms were employed to assess the adsorption behavior of the silver oxide impregnated fly ash for MTBE removal in aqueous medium. The choice of silver oxide impregnated fly ash was due to the significant improvement in adsorption it achieved over the other ash based adsorbent materials prepared and used in this study. Langmuir (1916) isotherm model, which explains the monolayer adsorption, suggesting that adsorbent materials have a finite capacity, regarded as the equilibrium state, which is the point beyond which no further adsorption take place. The existence of specific homogenous sites within the adsorbent at which adsorption occurs is it main assumption. The Langmuir isotherm is expressed by the equation below;

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad - - - - - - - \quad (3)$$

The above equation can be linearized to

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}} \quad - - - - - - - \quad (4)$$

From the above equations, C_e is the equilibrium MTBE concentration (mg/L); q_e is amount of MTBE (mg) adsorbed per gram of the adsorbent at equilibrium (mg/g); q_{max} is the theoretical maximum adsorption capacity (mg/g) and K_L is the Langmuir isotherm constant (L/mg). A linear plot of $1/q_e$ against $1/C_e$ was used to obtain the values of q_{max} and K_L from the slope and intercept.

The Freundlich isotherm model was the second model applied in this study, to explain the adsorption behavior of the adsorbent material. Adsorption on heterogeneous surfaces with interaction between adsorbate molecules being the main application of this model. An exponential fall in adsorption energy upon completion of adsorbents' sorption centers is the main assumption of this model (Crini and Badot, 2008). The Freundlich isotherm is express by the equation below;

$$q_e = K_F C_e^{1/n} \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad (5)$$

The above equation can be linearized to

$$ln\ q_e = ln\ K_F + \frac{1}{n}\ ln\ C_e \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad (6)$$

From the above equations, C_e is the equilibrium MTBE concentration (mg/L); q_e is amount of MTBE (mg) adsorbed per gram of the adsorbent at equilibrium (mg/g); K_F is the Freundlich adsorption constant related to the adsorbent adsorption capacity [(mg/g)(L/mg)$^{1/n}$]. A linear plot of lnq_e against lnC_e was used to obtain the values of K_F and n from the intercept and slope respectively. Plots from Figures 4.27 and 4.28 show that the adsorption of MTBE onto silver oxide impregnated fly ash conformed better to the Langmuir isotherm model, having a correlation co-efficient closer to unity.

Table 4.2: Isotherm parameters from MTBE adsorption using silver oxide impregnated fly ash

Parameters	**Langmuir Model**					
	Equation	Slope	R^2	Intercept	q_{max} (mg/L)	K_L (L/mg)
	y= 13.35x - 16.65	13.35	0.9875	-16.65	0.48	-1.2472
	Freundlich Model					
	Equation	Slope	R^2	Intercept	K_F (mg/g)	n
	y = 0.0561x - 0.2891	0.0561	0.7822	-0.2891	0.514	17.825

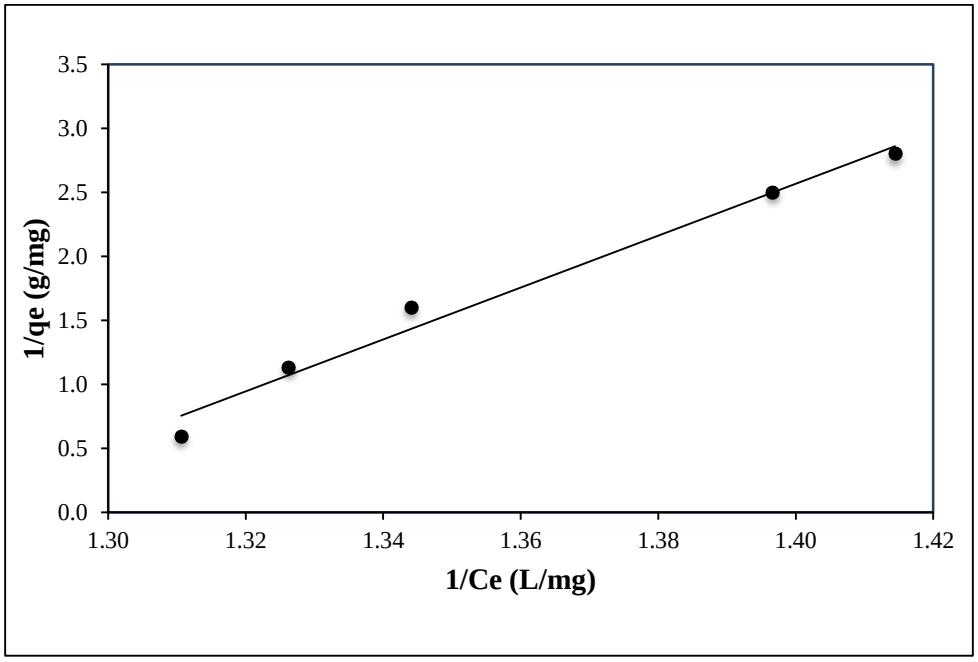


Figure 4.27: Langmuir isotherm plot of the adsorption of MTBE by silver oxide impregnated fly ash

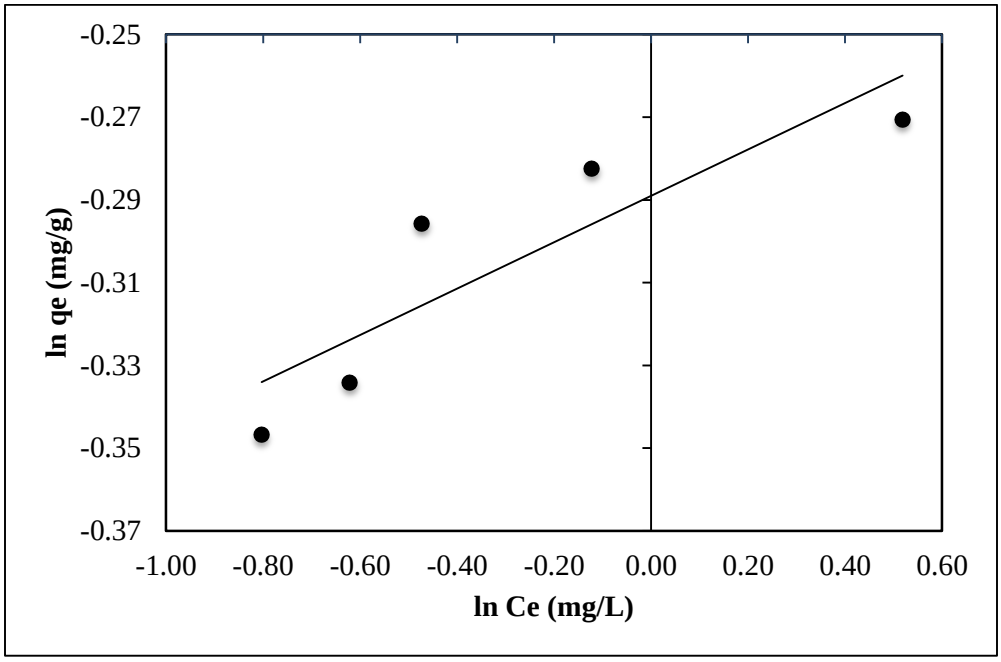


Figure 4.28: Freundlich isotherm plot of the adsorption of MTBE by silver oxide impregnated fly ash

4.8 Treatment Costs Estimates Comparison

From the removal efficiency point, activated carbon showed greater removal for MTBE when compared to the impregnated fly ash adsorbent material. However, depending on the intended use to which the treated water is meant to be applied the fly ash material may be a more viable option. For the estimation of costs, the total cost associated with MTBE removal from aqueous solution was divided into the fixed costs and variable costs. Fixed costs being those costs that remain constant irrespective of the adsorbent material used, while variable costs are those likely to change with variation in the adsorbent material.

Fixed costs in this case include the power cost, personnel cost, and treatment unit cost. While variable costs include the cost of the adsorbent materials, preparation costs, and additives cost. By calculating the amount of MTBE adsorbed per gram of adsorbent material, the adsorbent material requirement was established. Given that the optimum dosage for the silver oxide impregnated fly ash was 50 mg of adsorbent material, 50 mg of activated carbon was used for comparison. Using the formula for q_e computation stated in equation 1,

$$q_e = \frac{\mathrm{V}}{m}\,(C_O - C_{\mathrm{e}}),$$

With 100mL aqueous solution, 50mg of adsorbent material and 1000 µg/L initial MTBE concentration, we compute q_e for both adsorbent materials. For silver oxide impregnated fly ash, 24% was the optimum reduction in MTBE concentration achieved in 2 hours of contact, while 33% reduction in MTBE concentration was achieved with the use of

activated carbon. Using the formula above, at the optimum percentage reductions, 0.48 mg of MTBE would be removed per gram of silver oxide impregnated fly ash and 0.66 mg of MTBE per gram of activated carbon. At an estimated average cost of SR2.25 per gram of silver nitrate required for fly ash impregnation and SR0.05 per gram for activated carbon, it can be assumed that in terms of material costs, approximately SR0.1 is required to remove 1.0 mg of MTBE in a contaminated system using activated carbon, while SR0.46 will be required to remove 1.0 mg of MTBE when silver oxide impregnated fly ash is used, based on the assumption that the fly ash material is a free waste and not considering the additional costs associated with the impregnation process. Based on the above, it is more economical to use activated carbon as adsorbent material. However, from a waste management point of view, the use of fly ash material cannot be totally discounted. This is because the cost comparison cannot be limited to only the cost of preparation of the silver oxide impregnated fly ash materials. It is important to recognize the potential cost of waste disposal associated with the disposal of the fly ash, usually by landfilling, noting the capital intensive nature of landfills construction. As such, it is considered environmentally friendly to continue to seek out ways to reuse the tones of fly ash generated annually from the combustion of heavy liquid fuel during the generation of the electricity.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The objective of this study was to assess the potential of fly ash as an adsorbent of MTBE in aqueous solution. The goal was to understand how the adsorption process might be influenced by several experimental variables and obtain a set of optimum conditions under which the best possible removal of MTBE from aqueous solution can be achieved.

From evidences in literature search, fly ash had successfully been applied for the removal of a number of contaminants such as dyes, heavy metals and phenolic compounds from aqueous solution. The major motivations of this study were these successes recorded from the use of fly ash and the potential for waste management in the process of treating a contaminated system. The results from this study showed that the non-modified fly ash was unable to achieve significant removal of MTBE from aqueous solution, as less than 10% reduction in MTBE concentration was achieved for both the raw fly ash and the fly ash following acid treatment. Contrary to the case of the non-modified fly ash, modified fly ash showed limited success in MTBE removal for the silver oxide impregnated fly ash, where a 24% MTBE removal efficiency was achieved. However, similar modifications with aluminum oxide and ferric oxide failed to yield desired results, as less than 15% MTBE removal efficiency was achieved in both cases. The role of experimental variables such as pH was also assessed in this work, with the non-modified

fly ash showing no significant variation in adsorption behavior at all the pH studied ranging 3 to 9. However, the silver oxide impregnated fly ash showed increase in MTBE removal efficiency with decrease in pH, with the highest removal efficiency of 37% at pH 3. No further study was conducted at this pH because the work was designed for treatment at the pH of the region's groundwater (6 ± 0.5) and a removal of 24% was achieved at this pH level. Given the successful removal of MTBE by silver oxide impregnated fly ash, further work was conducted on this adsorbent material, and the optimum conditions required were found to be 50 mg dosage for 1000 µg/L initial MTBE concentration in aqueous solution, 200rpm agitation speed and a contact time of 2 hours.

To further understand the adsorption behavior of the fly ash material, a synergistic approach was adopted, where a combination of activated carbon and various fly ash materials were utilized, to assess whether the fly ash material could enhance the overall MTBE removal efficiency of activated carbon. From the results obtained, the raw fly ash was unable to make any notable contribution to MTBE removal using activated carbon, as the results from activated carbon alone showed better removal than the combination. Similarly, ferric oxide impregnated fly ash was unable to enhance the removal efficiency of activated carbon, rather it brought about a slight reduction in its removal efficiency. However, in the case of silver oxide impregnated fly ash, there was no reduction in the removal efficiency of the activated carbon, although the result from the combination was not significantly different from activated carbon alone, indicating possible masking of the functioning of the silver oxide impregnated fly ash by the activated carbon. Given the adsorption behavior of fly ash following silver oxide impregnation, a study of the behavior of activated carbon under similar condition was conducted. The result which

showed a drop from 71% to 53% in removal efficiency of activated carbon following impregnation with silver oxide. This observation lead to the conclusion that for a low surface area material like fly ash, impregnation with silver oxide brought about an increase in the surface area and adsorption sites, hence the improvement in MTBE removal efficiency. However, for a high surface area material like activated carbon, the silver oxide impregnation brought about a reduction in surface area and available adsorption sites, hence the decline in its removal efficiency. The potential of fly ash as a cost efficient adsorbent for the removal of MTBE from aqueous solution is presented in these experimental results and the fly ash showed low to intermediate removal efficiency.

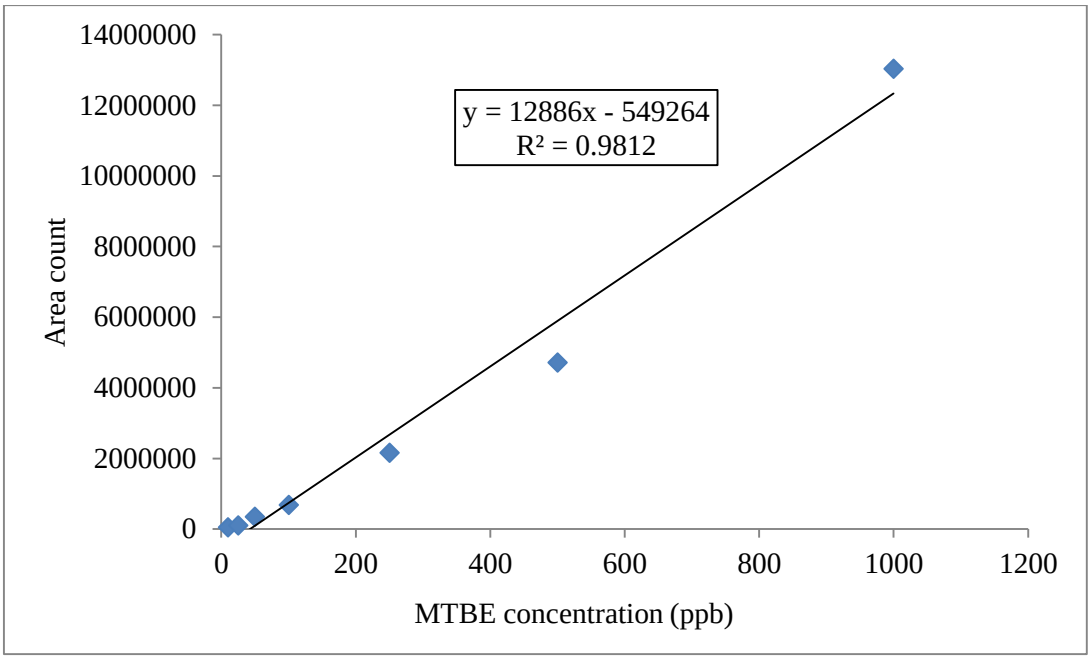
5.2 Recommendations

In order to add to scientific knowledge in this area of research and build upon the findings made in this study, the following recommendations are made;

1. Further studies on other modifications to fly ash that could bring about higher adsorption efficiency than achieved with silver oxide impregnation in this study.
2. Subsequent studies on the combination of both non-modified and modified fly ash with other established MTBE treatment techniques, to assess potential improvement of their treatment efficiencies.
3. Application of similar adsorbent materials as used in this study on a different contaminant of environmental concern.

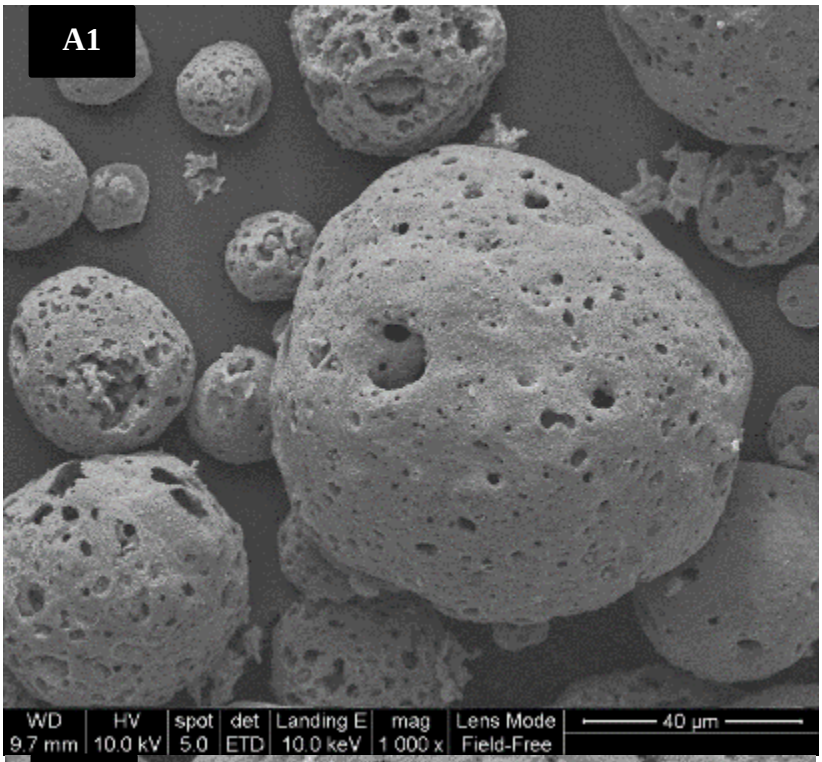
APPENDICES

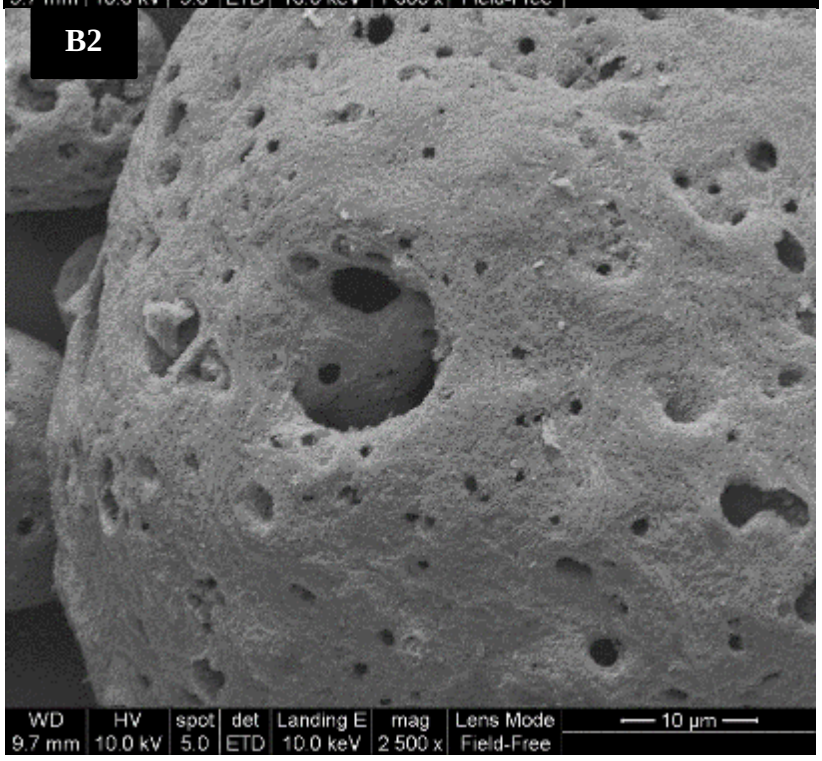
APPENDIX A: CALIBRATION CURVE



A) MTBE calibration curve

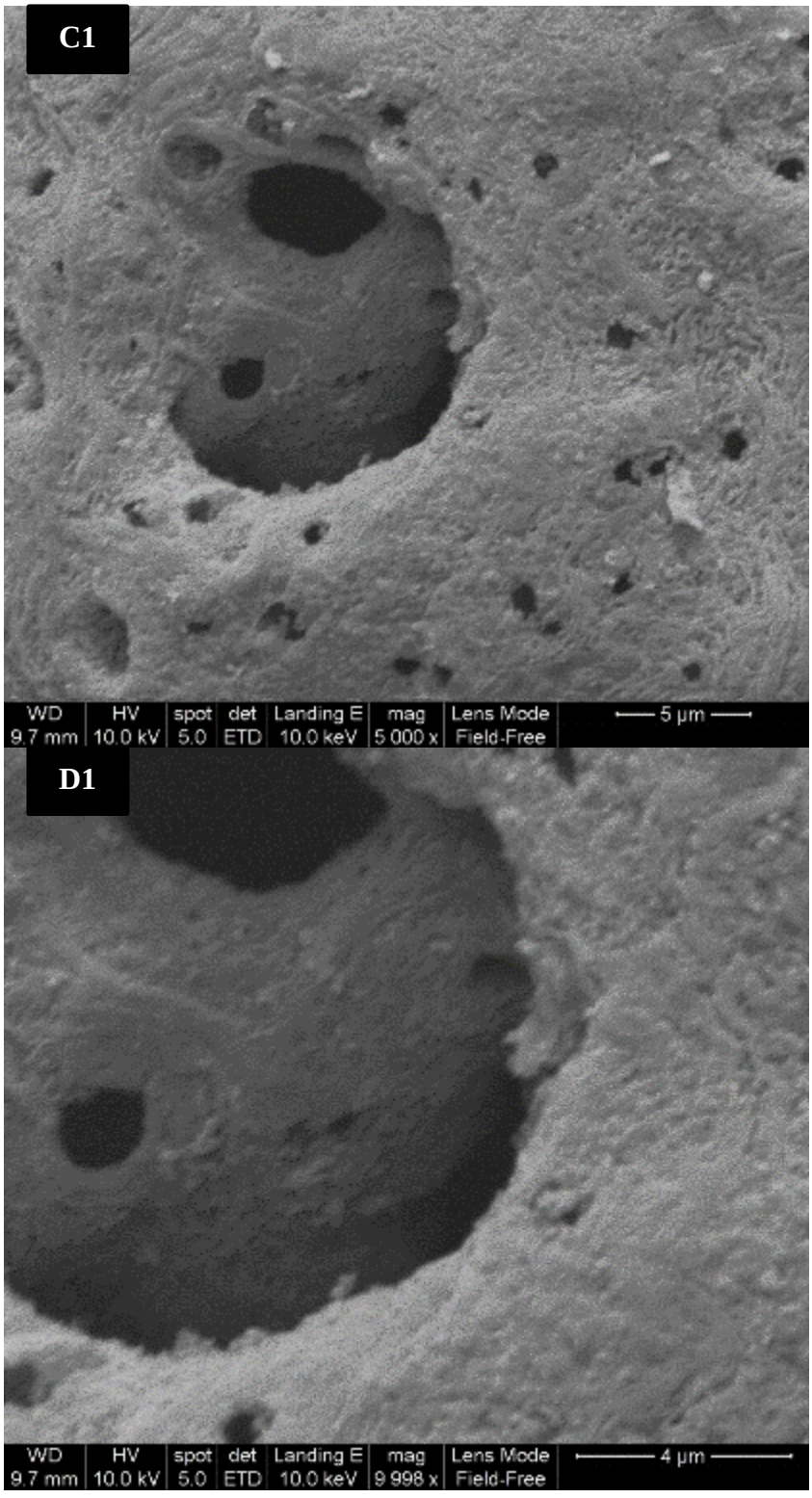
APPENDIX B: SEM MICROGRAPHS





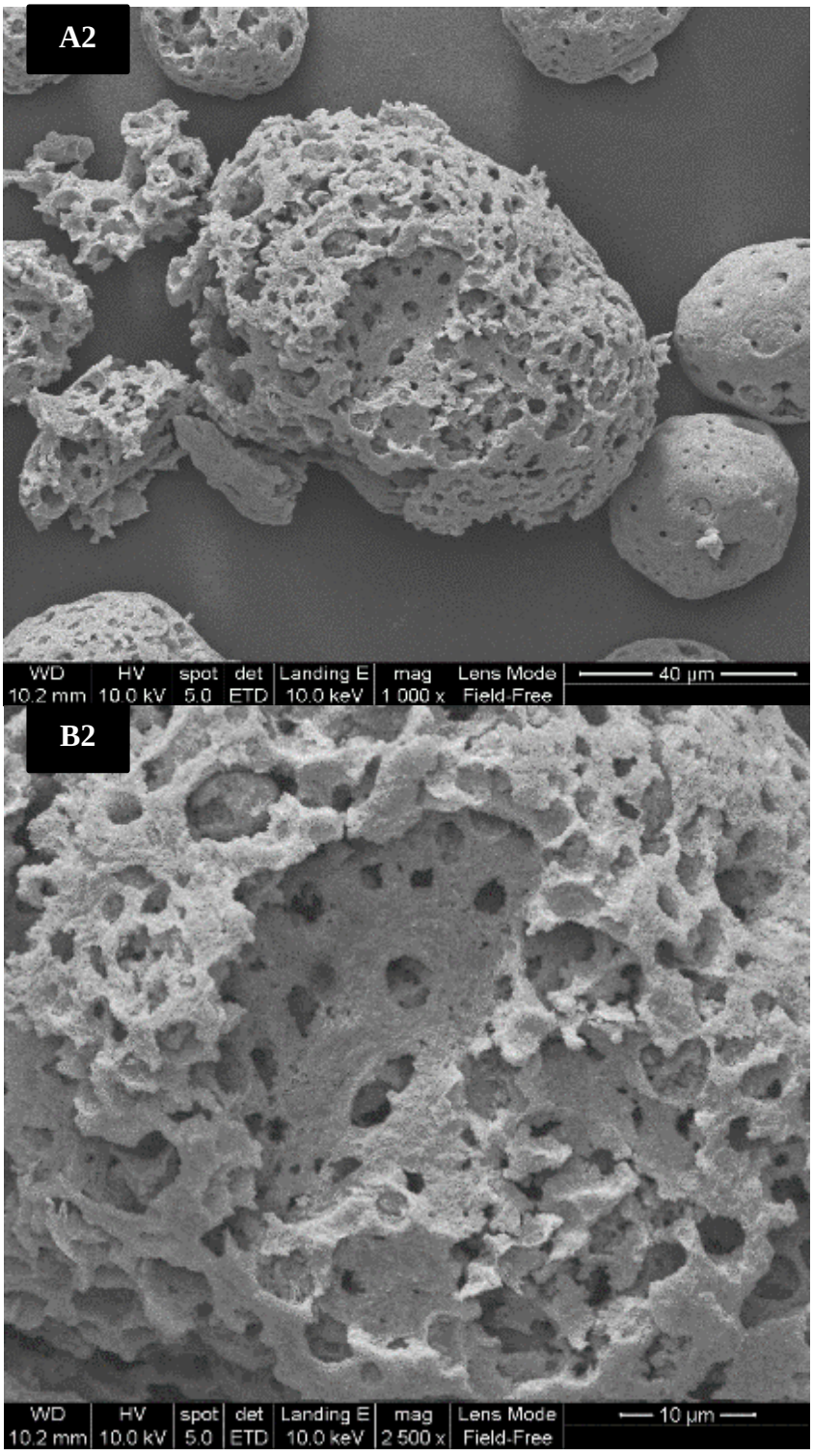
A1) SEM micrograph of raw fly ash (magnification x 1000)

B1) SEM micrograph of raw fly ash (magnification x 2500)



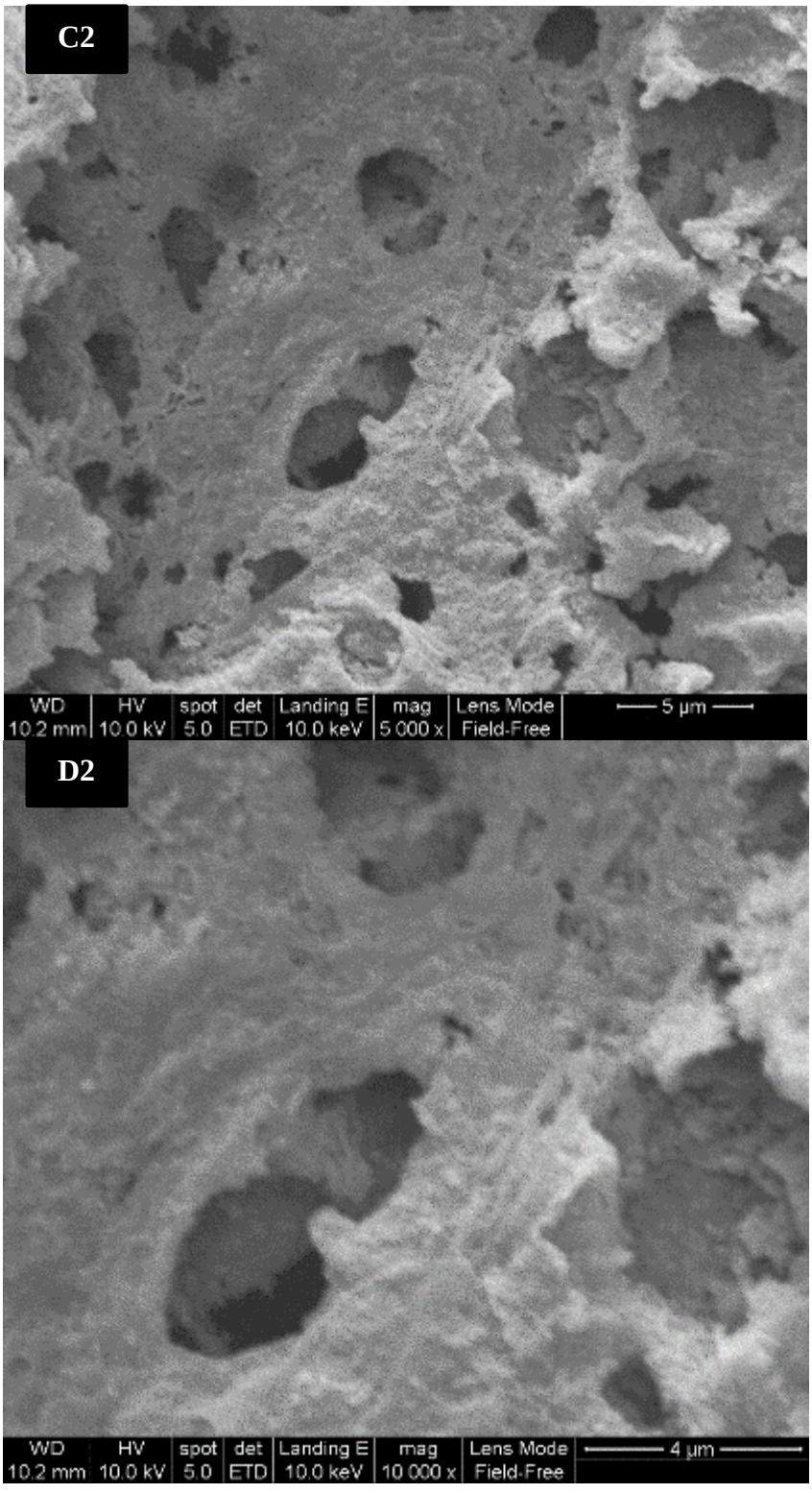
C1) SEM micrograph of raw fly ash (magnification x 5000)

D1) SEM micrograph of raw fly ash (magnification x 10000)



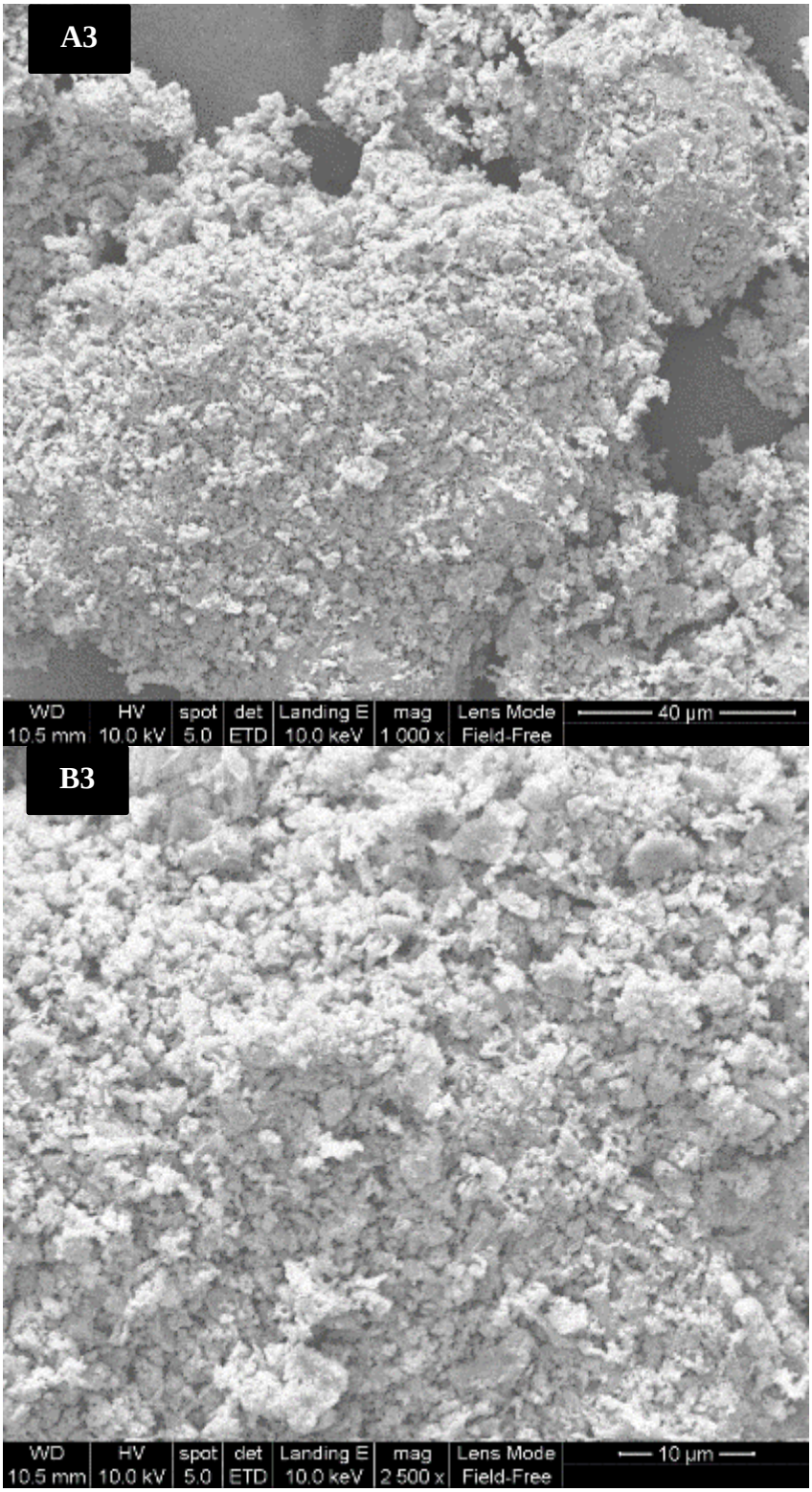
A2) SEM micrograph of acid treated fly ash (magnification x 1000)

B2) SEM micrograph of acid treated fly ash (magnification x 2500)



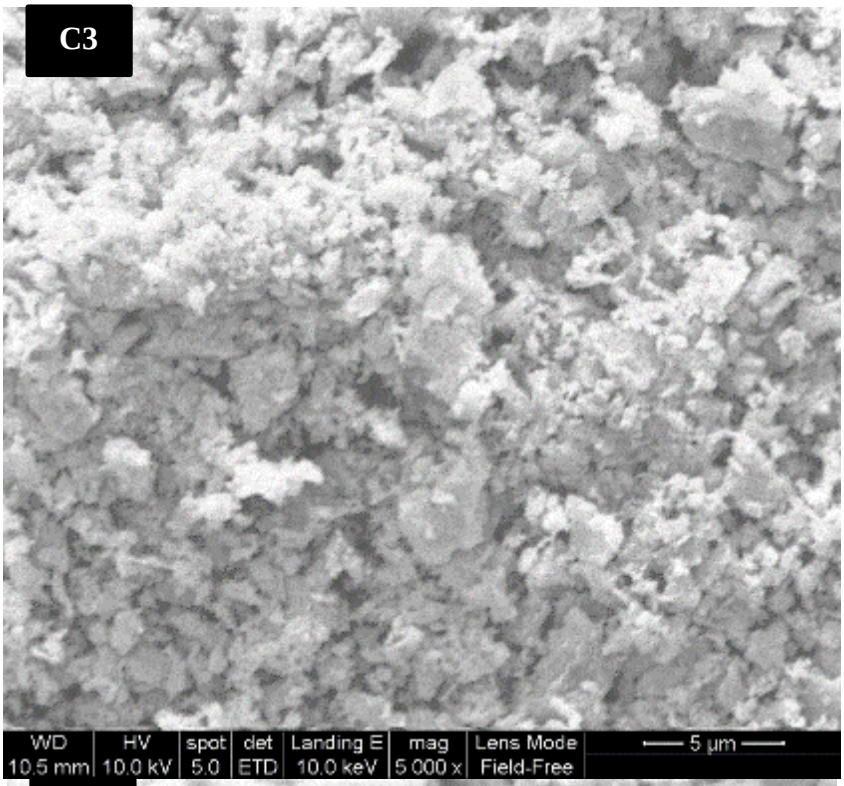
C2) SEM micrograph of acid treated fly ash (magnification x 5000)

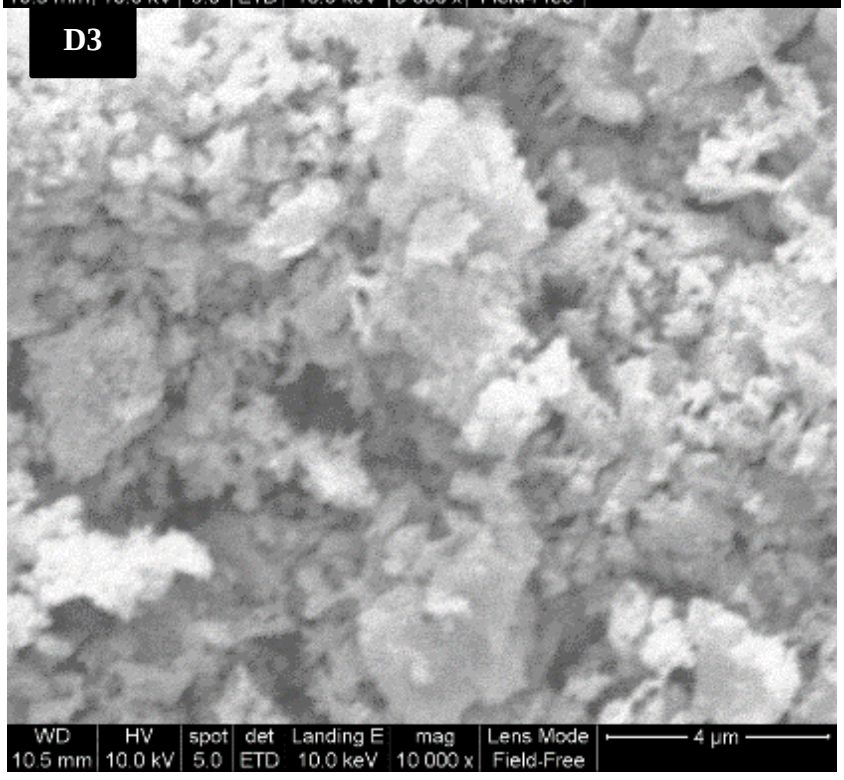
D2) SEM micrograph of acid treated fly ash (magnification x 10000)



A3) SEM micrograph of silver oxide impregnated fly ash (magnification x 1000)

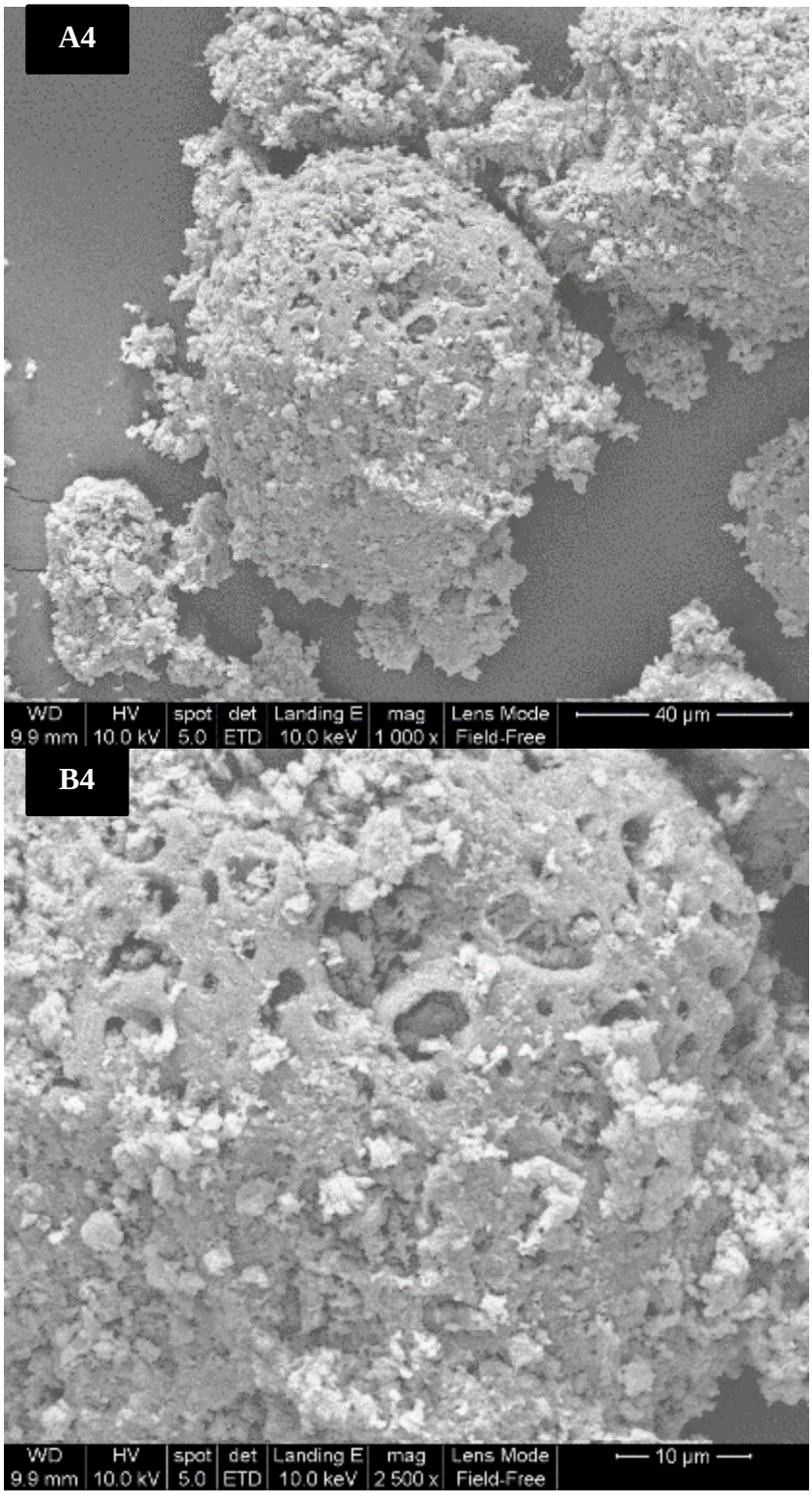
B3) SEM micrograph of silver oxide impregnated fly ash (magnification x 2500)





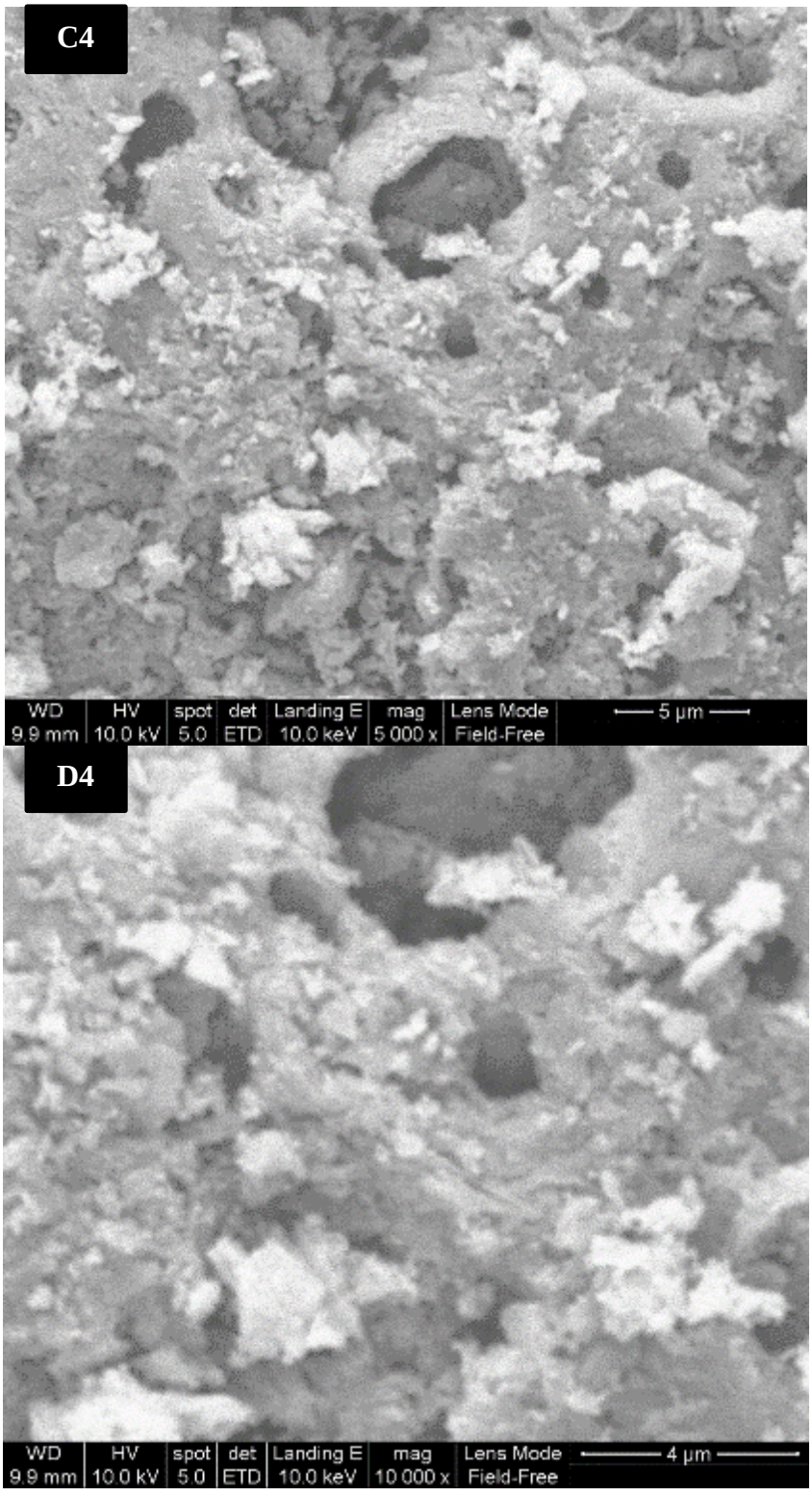
C3) SEM micrograph of silver oxide impregnated fly ash (magnification x 5000)

D3) SEM micrograph of silver oxide impregnated fly ash (magnification x 10000)



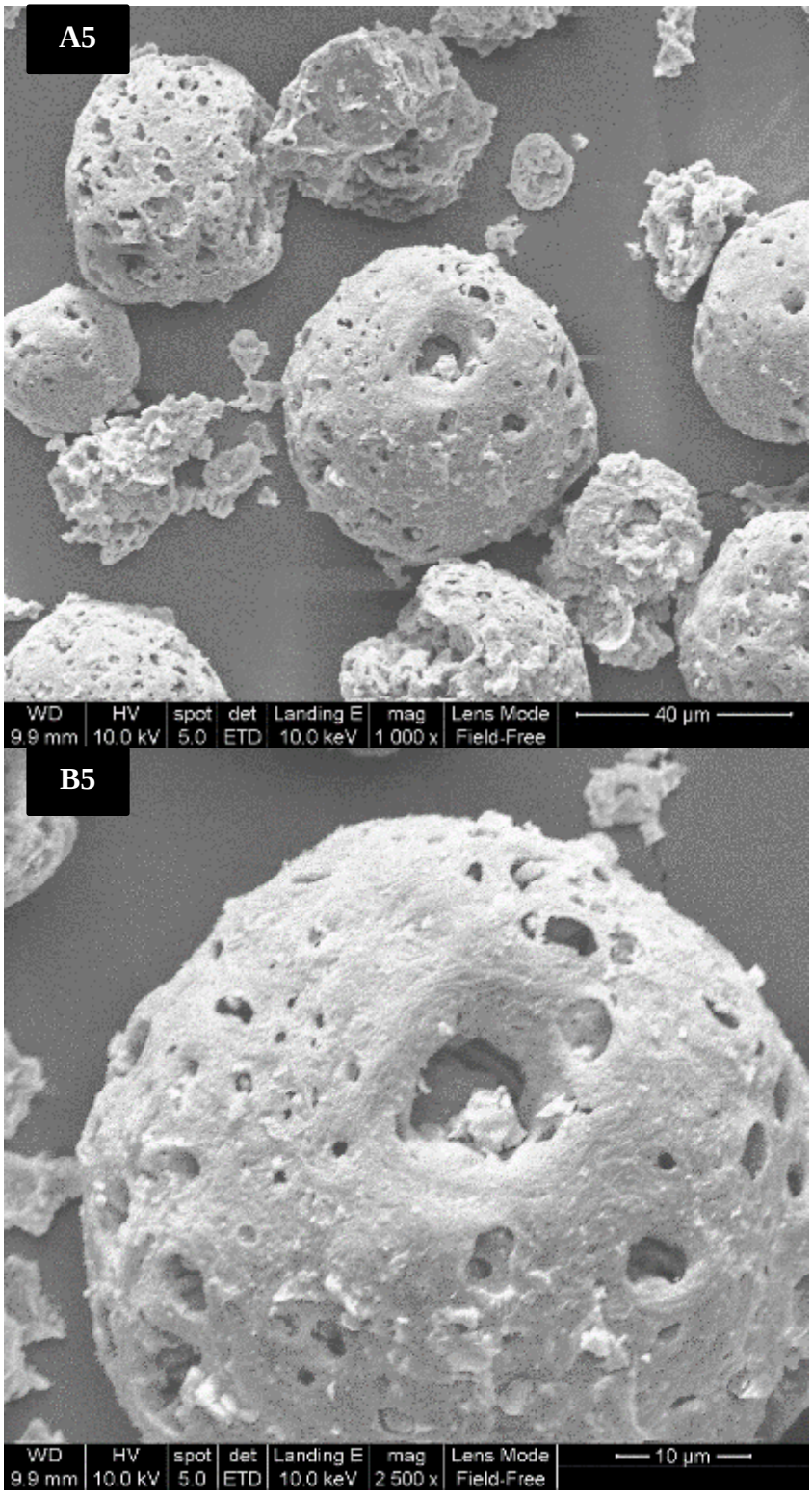
A4) SEM micrograph of ferric oxide impregnated fly ash (magnification x 1000)

B4) SEM micrograph of ferric oxide impregnated fly ash (magnification x 2500)



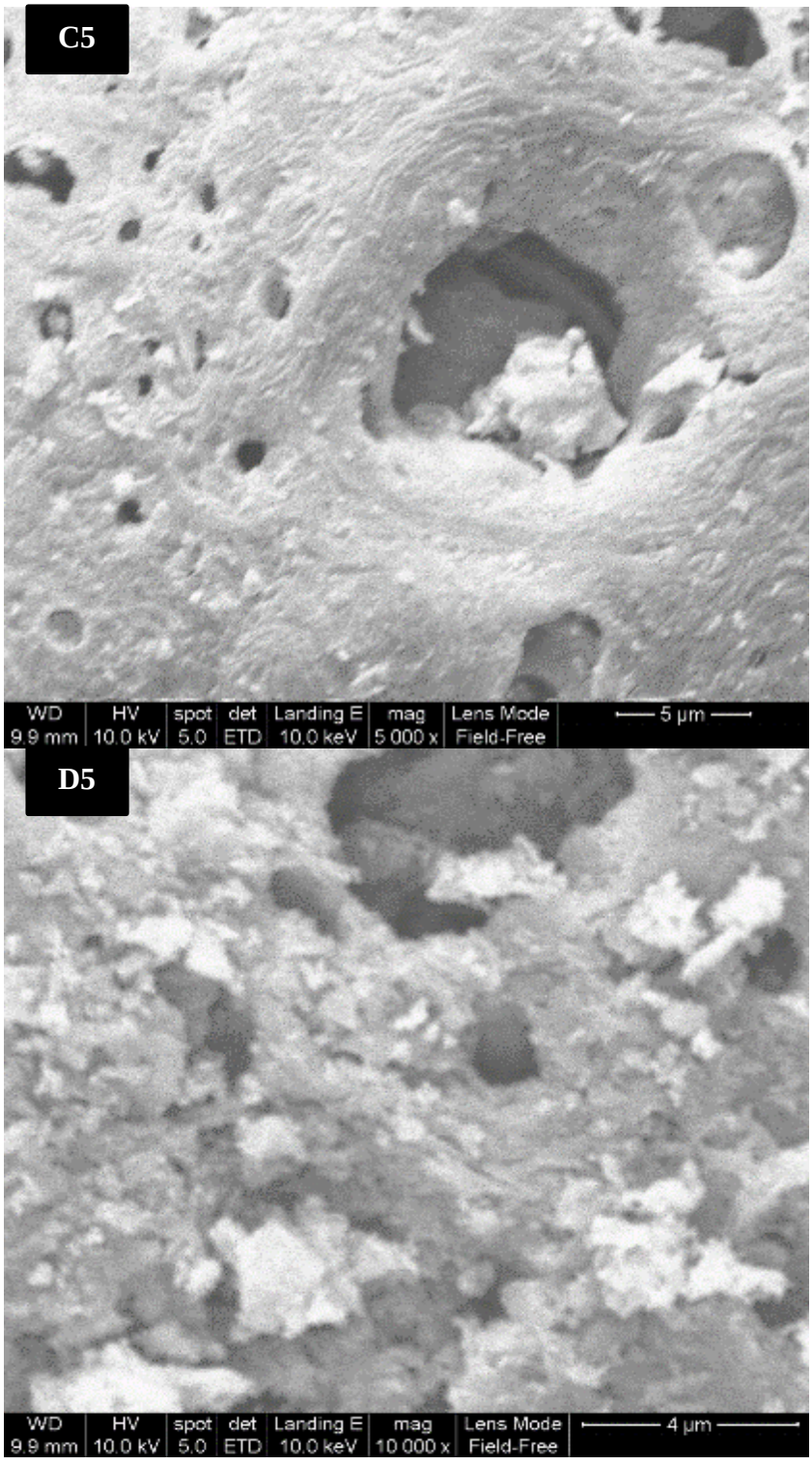
C4) SEM micrograph of ferric oxide impregnated fly ash (magnification x 5000)

D4) SEM micrograph of ferric oxide impregnated fly ash (magnification x 10000)



A5) SEM micrograph of aluminum oxide impregnated fly ash (magnification x 1000)

B5) SEM micrograph of aluminum oxide impregnated fly ash (magnification x 2500)



C5) SEM micrograph of aluminum oxide impregnated fly ash (magnification x 5000)

D5) SEM micrograph of aluminum oxide impregnated fly ash (magnification x 10000)

APPENDIX C: ADSORPTION ISOTHERM DATA

Temperature	25 ± 3°C							
Contact time	2 hours							
Adsorbent Mass (g)	**MTBE initial (mg/L)**	**Volume (L)**	**C_e (mg/L)**	**q_e (mg/g)**	**$1/C_e$ (L/mg)**	**1/qe (g/mg)**	**ln qe (mg/g)**	**ln Ce (mg/L)**
0.010	0.931	0.1	0.763	1.68	1.31	0.6	0.52	-0.27
0.020	0.931	0.1	0.754	0.89	1.33	1.1	-0.12	-0.28
0.030	0.931	0.1	0.744	0.62	1.34	1.6	-0.47	-0.30
0.040	0.931	0.1	0.716	0.40	1.40	2.5	-0.62	-0.33
0.050	0.931	0.1	0.707	0.35	1.41	2.8	-0.80	-0.35

REFERENCES

American Cancer Society (2011), Methyl Tertiary Butyl Ether (MTBE), http://www.cancer.org/cancer/cancercauses/othercarcinogens/pollution/mtbe

Agency for Toxic Substances and Disease Registry (ATSDR), (1996). Toxicological profile for methyl tert-butyl ether (MTBE), Atlanta, GA: *U.S. Department of Health and Human Services, Public Health Service.*

Aivalioti M., Papoulias P., Kousaiti A., and Gidarakos E., (2012a). Adsorption of BTEX, MTBE and TAME on natural and modified diatomite. *J Hazard Mater;* 207–208:117–27.

Akgerman A. and Zardkoohi M., (1996). Adsorption of Phenolic Compounds on Fly Ash, *Journal of Chemical and Engineering Data;* 41 (2):185 – 187

Aksu Z., and Yener J., (2001). A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents, *Waste Manage*; 21 (8):695–702

Anderson L., (1994). Methyl Tertiary-Butyl Ether Risk Management 1 Screening Document, (Draft), *Chemical Screening and Risk Assessment Division, U.S. EPA, Washington, DC.*

Anderson M.A., (2000). Removal of MTBE and other organic contaminants from water by sorption to high silica zeolites. *Environ Sci Technol*; 34:725–7.

Arletti R., Martucci A., Alberti A., Pasti L., Nassi M., and Bagatin R., (2012). Location of MTBE and toluene in the channel system of the zeolite mordenite: adsorption and host–guest interactions. *J Solid State Chem*; 194:135–42.

Barreto R.D., Gray K.A., and Anders K., (1995). Photocatalytic degradation of methyl-tert-butyl ether in TiO2 slurries: a proposed reaction scheme. *Water Res*; 29:1243–8

Baus C., Sona M., and Brauch H.J., (2007). Ozonation and combined ozone/H2O2, UV/ozone and UV/H2O2 for treatment of fuel oxygenates MTBE, ETBE, TAME, and DIPE from water—a comparison of removal efficiencies. *Water Sci. Technol.;* 55:307–11.

Bertelli M., and Selli E., (2004). Kinetic analysis on the combined use of photocatalysis, H_2O_2 photolysis, and sonolysis in the degradation of methyl tert-butyl ether, Applied Catalysis B: *Environmental;* 52:205-212.

Burbano A.A., Dionysiou D.D., Suidan M.T., and Richardson T.L., (2005). Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent, *Water Research*; 39:107-118.

Burghoff B., Sousa Marques J., van Lankvelt B.M., and de Haan A.B., (2010). Solvent impregnated resins for MTBE removal from aqueous environments. *React Funct Polym*; 70:41–7.

Cater S.R., Stefan M.I., Bolton J.R., and Safarzadeh-Amiri A., (2000). UV/H_2O_2 treatment of methyl iert-butyl ether in contaminated waters, *Environ. Sci. Technol*; 34:659-662.

Chang P.B.L., and Young T.M., (2000). Kinetics of Methyl Tert-Butyl Ether Degradation and By-Product Formation during UV/Hydrogen Peroxide Water Treatment, *Water Research*; 34(8):2233-2240.

Chen D.Z., Zhang J.X., and Chen J.M., (2010). Adsorption of methyl tert-butyl ether using granular activated carbon: equilibrium and kinetic analysis. *Int J Environ Sci Technol* (IJEST); 7:235–42.

Crini G., and Badot P.M., (2008). Application of chitosan, a natural amino polysaccharide for dye removal from aqueous solutions by adsorption process using batch studies: a review of recent literature, *Progress in Polymer Science;* 33:399–447.

Damm J.H., Hardacre C., Kalin R.M., and Walsh K.P., (2002). Kinetics of the oxidation of methyl tert-butyl (MTBE) by potassium permanganate, *Water Research;* 36(14):3638-3646.

Davis S.W., and Powers P.E., (2000). Alternative sorbents for removing MTBE from gasoline-contaminated ground water. *J Environ Eng;* 126:354–60.

Deeb R.A., Scow K.M., and Alvarez-Cohen A., (2000). Aerobic MTBE biodegradation: an examination of past studies, current challenges and future directions. *Biodegradation*; 11:171–86

Deeb R., Hawley E., Stocking A., Kavanaugh M., Flores A., Sue S., et al., (2006). Removal of MTBE from drinking water using air stripping: case studies.

Diels L., and Lookman R., (2007). Microbial systems for in-situ soil and groundwater remediation. In: Marmiroli N, Samotokin B, Marmiroli M, editors. Advanced science and technology for biological decontamination of sites affected by chemical and radiological nuclear agents. *Dordrecht, The Netherlands: Springer*; 61–77

El-Sayed, G.O., (2011). Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber. *Desalination;* 272:225–232.

Eslami A., Nasseri S., Yadollahi B., Mesdaghinia A., Vaezi F., Nabizade R., et al., (2008). Photocatalytic degradation of methyltert-butyl ether (MTBE) in contaminated water by ZnO nanoparticles. *J Chem Technol Biotechnol*; 83:1447–53

Fierro J.L., (Ed.). (2005). *Metal Oxides: chemistry and applications*. CRC press.

Fujiwara Y., Kinoshita T., Sato H., and Kojima I., (1984). Biodegradation and bioconcentration of alkylethers. *Yukagaku;* 33:111-114

Georgi A., and Kopinke F.D., (2005). Interaction of adsorption and catalytic reactions in water decontamination processes: Part I. Oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon, *Applied Catalysis B: Environmental*; 58(1/2):9-18.

Graham J.L., Striebich R., Patterson C.L., Radha Krishnan E., and Haught R.C., (2004). MTBE oxidation byproducts from the treatment of surface waters by ozonation and UV-ozonation. *Chemosphere*; 54:1011–6

Ghadiri S.K., Nabizadeh R., Mahvi A.H., Nasseri S., Kazemian H., and Mesdaghinia A.R., (2010). Methyl tert-butyl ether adsorption on surfactant modified natural zeolites. *Iran J Environ Health Sci Eng;* 7:241–52.

Hassen J.A., and Gross C.P., (2000). MTBE: groundwater remediation technologies. *Remediat J;* 10:129–30

Hazardous Substances Data Bank (HSDB), (1994). MEDLARS Online Information Retrieval System, *National Library of Medicine*.

Howard P.H., Sage G.W, Jarvis W.E., and Gray D.A., (1990). Handbook of environmental fate and exposure data for organic chemicals, Volume IV: *Chelsea, Mich., Lewis Publishers, Inc.,* 578

Hsieh L.L., Lin Y.L., and Wu C.H., (2004). Degradation of MTBE in dilute aqueous solution by gamma radiolysis, *Water Research*; 38(16):3627-3633.

Hung H., and Lin T., (2006). Adsorption of MTBE from contaminated water by carbonaceous resins and mordenite zeolite. *J Hazard Mater;* 135:210–7.

Hu Q., Zhang C., Wang Z., Chen Y., Mao K., Zhang X., et al., (2008). Photodegradation of methyl tert-butyl ether (MTBE) by UV/H2O2and UV/TiO2. *J Hazard Mater;* 154:795–803.

Inal F., Yetgin S., Aksu G.T., Simsek S., Sofuoglu A., and Sofuoglu S.C., (2009). Activated carbon adsorption of fuel oxygenates MTBE and ETBE from water. *Water Air Soil Pollution;* 204:155–63.

Induchny S., Archibald J., and Mulica W.S., (2005). Use of in-situ oxygen curtain technology in enhanced bioremediation of groundwater. In: Omelchenko A, Pivovarov AA, Swindall WJ, editors. Modern tools and methods of water treatment for improving living standards. *The Netherlands: Springer*; 109–13

Iob A., Buenafe R., and Abbas N.M., (1998). Determination of oxygenates in gasoline by FTIR. *Fuel*; *77*(15):1861-1864.

Jacobs J., Guertin J., and Herron C., (2000). MTBE: Effects on Soil and Groundwater *Resources: Lewis Publishers, Inc. Boca Raton, FL*.

Jensen H.M., and Arvin E., (1990). Solubility and degradability of the gasoline additive MTBE and gasoline compounds in water. In: Arendt F, Hinsenveld M, Van den Brink WJ (eds) Contaminated soil, 90. Kluwer, *Dordrecht*; 445-448

Kannan N., and Sundaram M.M., (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons – a comparative study. *Dyes and Pigments;* 51:25–40.

Keller A.A., Bierwagen B., Sirivithayapakorn S., and Kram M., (1999). Advances in Groundwater Treatment to Remove MTBE, Paper presented at the *31st Mid-Atlantic Industrial and Hazardous Waste Conference, University of Connecticut, Storrs, CT.*

Kelley Q. K., (2004). The economic effect of governmental incentives on the ethanol fuel market (Doctoral dissertation, uga).

Kinner N.E., (2001). Fate, Transport, and Remediation of MTBE: Testimony before the United States Senate Committee on Environment and Public Works. Salem, NH.

Langmuir I., (1916). The constitution and fundamental properties of solids and liquids. *Journal of American Chemical Society;* 38:2221–2295.

Laohaprapanon S., Marques M., and Hogland W., (2010). Removal of Organic Pollutants from Wastewater Using Wood Fly Ash as a Low-Cost Sorbent, *CLEAN – Soil, Air, Water;* 38, (11):1055–1061

Li L., Quinlivan P.A., and Knappe D.R.U., (2002). Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. *Carbon*; 40:2085–100.

Li Y., Liu Y., Deng H., and Zhang S., (2012). The adsorption and desorption characteristics of a novel sorbent in groundwater remediation: modified oil sludge. *Adv Mater Res;* 599:412–7.

Lien H.L., and Zhang, W., (2002). Novel Bifunctional Aluminum for Oxidation of MTBE and TAME, *Journal of Environmental Engineering*; 128(9):791-798.

Mackay W.Y., Donald W.Y., Shiu W.Y., and Ma K.C., (1993). Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals—Volatile organic chemicals, *Volume III: Chelsea, Mich., Lewis Publishers, Inc.*, 916

Mahmoud S.A., and Sen Z., (1993). Regional Variations of Monthly Rainfall Amounts in the Kingdom of Saudi Arabia, *JKAU: Earth Science*; (6):113–133

Melin G., (2000). Treatment technologies for removal of methyl tert-butyl ether from drinking water.

Mitani M.M., Keller A.A., Bunton C.A., Rinker R.G., and Sandall O.C., (2002). Kinetics and products of reactions of MTBE with ozone and ozone/hydrogen peroxide in water. *J Hazard Mater*; 89:197–212

Mott H.V., and Weber Jr, W.J., (1992). Sorption of low molecular weight organic contaminants by fly ash: Considerations for the enhancement of cutoff barrier performance. *Environmental science & technology*; *26*(6):1234-1242.

Müller R.H., Rohwerder T., and Harms H., (2007). Carbon conversion efficiency and limits of productive bacterial degradation of methyltert-butyl ether and related compounds. *Appl Environ Microbiol*; 73:1783–91

Neppolian B., Jung H., Choi H., Lee J.H., and Kang J.W., (2002). Sonolytic degradation of methyl tert-butyl ether: the role of coupled fenton process and persulphate ion, *Water Research;* 36(19):4699-4708.

Patil S.L., Baride D.M., Husain D.M., and Mahajan B.V., (2010). Fly Ash Concrete For Road Pavement: A Techno-Economic Analysis. *International Journal of Advanced Engineering Technology* E-ISSN, 0976-3945.

Pirkanniemi K., and Sillanpää M., (2002). Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere*; 48:1047–60

Pirkanniemi K., Metsärinne S., and Sillanpää M., (2007). Degradation of EDTA and novel complexing agents in pulp and paper mill process and waste waters by Fenton's reagent. *J Hazard Mater*; 147:556–61

Rossner A., and Knappe D.R.U., (2008). MTBE adsorption on alternative adsorbents and packed bed adsorber performance. *Water Res;* 42:2287–99.

Ragheb S.M., (2013). Phosphate Removal from Aqueous Solution Using Slag and Fly ash, *Housing and Building National Research Center Journal*; 9:270–275.

Rick C., Barbara R., and John Z., (2001). National Survey of MTBE and other VOCs in Community Drinking-Water Sources, *U.S. Geological Survey*, FS-064-01

Santhi T., Manonmani S., and Smitha T., (2010). Removal of methyl redfrom aqueous solution by activated carbon prepared from theAnnona squamosa seed by adsorption. *Chemical Engineering Research Bulletin;* 14:11–18.

Salanitro J.P., Diaz L.A., Williams M.P., and Wisniewski H.L., (1994). Isolation of a bacterial culture that degrades MTBE. *Appl Environ. Microbiol;* 60:2593-2596

Salleh M.A.M., Mahmoud, D.K., Karim, W.A., and Idris, A., (2011). Cationic anionic dye adsorption by agricultural solid waste: a comprehensive review. *Desalination;* 280:1–13.

Saudi Basic Industries Corporation (2014). Facts and Figures. http://www.sabic.com/corporate/en/ourcompany/facts-and-figures

Seagren E.A., and Becker J.G., (2002). Review of natural attenuation of BTEX and MTBE in groundwater, *Pract. Period Hazard. Toxic. Radioact. Waste Manag.*; 6:156–172

Senthilkumar P., Ramalingam S., Senthamarai C., Niranjanaa M., Vijayalakshmi P., and Sivanesan S., (2010). Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination;* 261:52–60.

Schirmer M., Butler B.J., Barker B.J.F., Church C.D., and Schirmer K., (1999). Evaluation of biodegradation and dispersion as natural attenuation processes of MTBE and benzene at the Borden field site, *Phys. Chem. Earth* (B); 24:557–560

Shih T.C., Wangpaichitr M., and Suffet M., (2003). Evaluation of granular activated carbon technology for the removal of methyl tertiary butyl ether (MTBE) from drinking water. *Water Res.;* 37:375–85

Sim J., Seo H., and Kim C., (2009). Physicochemical characteristics for adsorption of MTBE and cadmium on clay minerals. *Environ Earth Sci;* 59:537–45.

Sontheimer H., Crittenden J.C., and Summers R.S., (1988). Activated carbon for water treatment. DVGW-Forschungsstelle (second ed.) Engler-Bunte-Institut, University of Karlsruhe, Karlsruhe, Germany

Sutherland J., Adams C., and Kekobad J., (2004). Treatment of MTBE by air stripping, carbon adsorption, and advanced oxidation: technical and economic comparison for five groundwaters, *Water Research*; 38(1):193-205.

Squillace P.J., Pope D.A., and Price C.V., (1995). Occurrence of the gasoline additive MTBE in shallow ground water in urban and agricultural areas, U.S. *Geological Survey* Fact Sheet FS-114-95, 4

Toxics Release Inventory 1992 (TRI92), (1994). Office of Pollution Prevention and Toxics, U.S. EPA, Washington, DC, [EPA745-R-94-001].

U.S. Environmental Protection Agency, (1993a). Technical Information Review: Methyl tertiary Butyl Ether (CAS No. 1634-04-4), Office of Pollution Prevention and Toxics, U.S. EPA, Washington, D.C.

U.S. Environmental Protection Agency, (1993c). Assessment of Potential Health Risks of Gasoline Oxygenated with Methyl Tertiary Butyl Ether (MTBE), Office of Research and Development, U.S. EPA, Washington, DC, [EPA/600/R-93/206].

U.S. Environmental Protection Agency, (1994). Chemical Summary for methyl-tert-butyl ether, Office of pollution prevention and toxics, [EPA 749-F-94-017a].

U.S. Environmental Protection Agency, (1997b). Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE). Washington, D. C.: U.S. Environmental Protection Agency, Office of Water, [EPA-822-F-97-009].

U.S. Environmental Protection Agency. (1998). Remediation of MTBE contaminated soil and groundwater; [EPA 510-F-98-002].

U.S. Environmental Protection Agency, (2000). Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions, Washington, D. C.: U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Subsurface Protection and Remediation Division, Coast Guard, Civil Engineering Unit, Office of Research and Development, [EPA/600/R-00/006].

U.S. Environmental Protection Agency, (2004). Monitored natural attenuation, in: How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers, [EPA 510-R-04-002].

Vilhunen S., Puton J., Virkutyte J., and Sillanpää M., (2011). Efficiency of hydroxyl radical formation and phenol decomposition using UV light emitting diodes and H2O2. *Environ Technol*; 32:865–72

Visa M., and Duta A., (2013a). TiO2/fly ash novel substrate for simultaneous removal of heavy metals and surfactants, *Chemical Engineering Journal*; 223:860–86

Visa M., and Duta A., (2013b). Methyl-orange and cadmium simultaneous removal using fly ash and photo-Fenton systems, *Journal of Hazardous Materials*; 244–245:773–779

Wang X., Deshusses M.A., (2007). Biotreatment of groundwater contaminated with MTBE: interaction of common environmental co-contaminants. *Biodegradation*; 18:37–50

Weber W.J., Mcginley P.M., and Katz L.E., (1991). Sorption phenomena in subsurface systems: concepts, model and effects on contaminant fate and transport. *Water Res.;* 25:499–528

Yadla S.V., Sridevi V., and Lakshmi C., (2012). Adsorption Performance of Fly Ash for the Removal of Lead, *International Journal of Engineering Research & Technology*; 1 (7):1-7.

Yeh C.K., and Novak J.T., (1994). Anaerobic biodegradation of gasoline oxygenates in soils, *Water Environ Res;* 66:744-752

Zhang A., Wang N., Jiang J. P., and Liu G., (2012). Heterogeneous Fenton-like catalytic removal of p-nitrophenol in water using acid-activated fly ash, *Journal of Hazardous Materials;* 201–202:68–73

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